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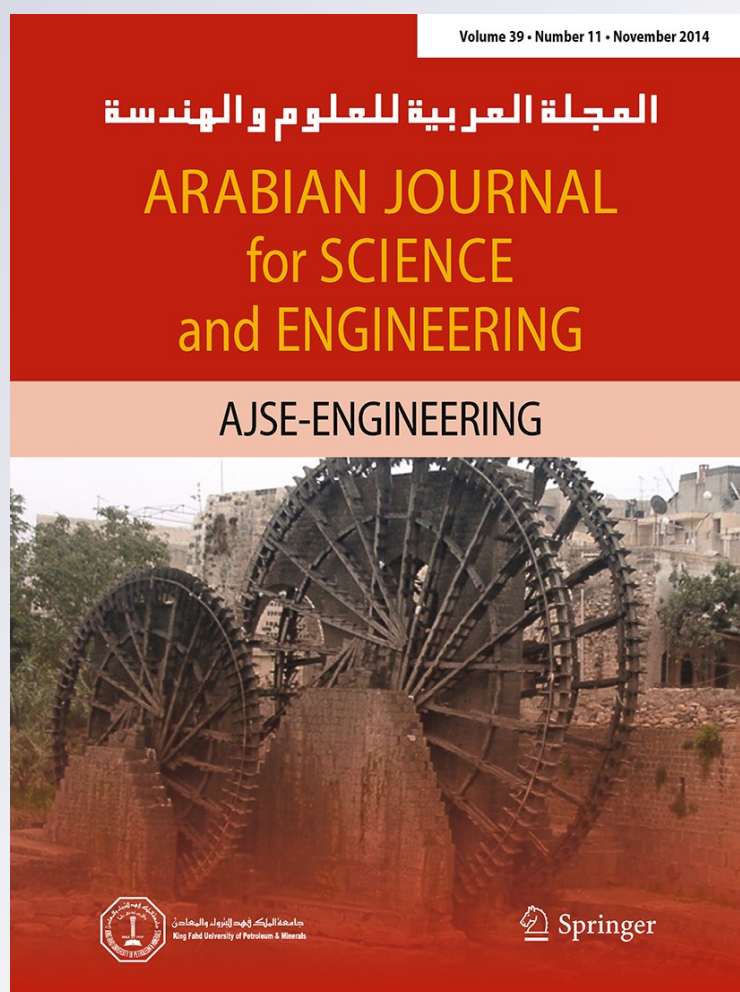
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# Inhibition of Copper Corrosion by Tolyltriazole in Cooling Systems Using Treated Municipal Wastewater as Makeup Water

Mahbuboor R. Choudhury · Radisav D. Vidic · David A. Dzombak

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**Abstract** Tolyltriazole (TTA) has been identified as an effective copper corrosion inhibitor in cooling systems using treated municipal effluent as makeup water. Significant removal of TTA from solution has been reported in previous studies in the presence of free chlorine and copper metal. Hence, for effective dosing of TTA in the cooling systems, it is important to understand the depletion scenario of TTA in solution in the presence of free chlorine and copper metal. In this study, TTA depletion in solution was assessed using batch reactor experiments in the presence of varying concentrations of free chlorine and copper metal in synthetic cooling water simulating treated municipal wastewater. Increasing free chlorine concentration resulted in more depletion of TTA from solution in the presence of copper metal, which may be due to more adsorption of TTA on to the cuprous oxide surface formed with enhanced corrosion of copper metal and to the formation of insoluble copper–TTA complex with the released copper ions in solution. The enhancement of copper metal corrosion in the presence of TTA and increasing concentration of free chlorine were assessed using electrochemical potentiodynamic polarization experiments. Also, TTA adsorption on cuprous oxide surface was assessed in batch reactor experiments. Packing density of TTA on cuprous

oxide surface was found to be pH dependent. More TTA was adsorbed onto cuprous oxide surface at higher pH values. Calculations of TTA free energy of adsorption showed that TTA was chemisorbed onto cuprous oxide.

**Keywords** Copper · Corrosion · Tolyltriazole · Polarization · Chlorine · Adsorption

## الخلاصة

تم تعريف التريازول باعتباره مثبّطاً لتآكل النحاس ذا فعالية في أنظمة التبريد باستخدام مياه الصرف المعالجة كمياه تعويض. وتم تسجيل إزالة مهمة للتريازول من المحلول في الدراسات السابقة في وجود الكلور الحر ومعدن النحاس. وبالتالي ولجرات فعالة من التريازول في أنظمة التبريد، فمن المهم أن نفهم سيناريو استنزاف التريازول في المحلول في وجود الكلور الحر ومعدن النحاس. وتم - في هذه الدراسة - تقييم استنزاف التريازول في محلول التجارب باستخدام دفعة في وجود تراكيز مختلفة من الكلور الحر ومعدن النحاس في مياه التبريد الاصطناعية كحاكاة لمياه الصرف المعالجة. وزيادة تركيز الكلور الحر أدى إلى المزيد من استنزاف التريازول من المحلول في وجود معدن النحاس الذي قد يكون راجعاً إلى امتزاز أكثر للتريازول على سطح أكسيد النحاس الذي تكون مع تعزيز تآكل معدن النحاس، وإلى تشكل معقد النحاس - التريازول غير قابلة للذوبان مع صدور أيونات النحاس في المحلول. وقد تم تقييم التعزيز في تآكل معدن النحاس في وجود التريازول وزيادة تركيز الكلور الحر باستخدام تجارب استقطاب الجهد الديناميكي الكهروكيميائية. وتم أيضاً تقييم امتزاز التريازول على سطح أكسيد النحاس في تجارب مفاعل الدفعة الواحدة. ووجد أن كثافة رص التريازول على سطح أكسيد النحاس هي تابعة للرقم الهيدروجيني. وقد امتز ترأيزول أكثر على سطح أكسيد النحاس عند قيم رقم هيدروجيني أعلى. وأظهرت حسابات طاقة امتزاز التريازول الحرة أن التريازول امتز كيميائياً فوق أكسيد النحاس.

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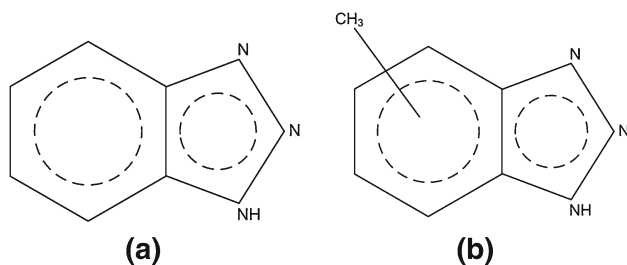
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## 1 Introduction

Use of treated municipal wastewater as makeup water results in degraded water quality in power plant recirculating cooling systems and makes corrosion management of such system





**Fig. 1** Chemical structure of **a** Benzotriazole, BTA and **b** Tolyltriazole, TTA (a mixture of 4- and 5-methylbenzotriazole)

even more challenging [1,2]. Different chemical regimens are used to control corrosion, scaling, and biofilm growth in cooling systems [2]. Copper alloys are frequently used as heat exchanger components in power plant cooling water systems due to its high heat exchange efficiency. Use of biocides (e.g., free chlorine) to control biofouling enhances the corrosion of copper alloys in heat exchangers [1,2]. Other cooling water properties, like pH, ammonia concentration also influence corrosion of copper alloys in cooling systems [1–3].

Tolyltriazole (TTA) and benzotriazole (BTA) have been recognized as effective copper corrosion inhibitors [4–8]. TTA ( $C_7H_7N_3$ ) is derived from BTA ( $C_6H_5N_3$ ) by substituting a methyl ( $-CH_3$ ) group in the benzene ring of BTA (Fig. 1). Presence of the methyl group in the benzene ring of TTA improves the surface coverage and thus improves the corrosion inhibition efficiency of TTA [9]. It has been reported that methyl substitution at position 4 and 5 on the benzene ring of BTA produces the most efficient TTA for copper and copper alloy corrosion inhibition [9]. The copper corrosion inhibition imparted by BTA and TTA is obtained through formation of a protective polymeric film of  $Cu(I)$ –BTA or  $Cu(I)$ –TTA, through chemisorption, on copper and copper alloy surfaces [9–11]. The triazole group is chemisorbed to surface copper atoms through sharing of the lone-pair electrons of the nitrogen atoms [12]. Several previous studies report experimental measurements of surface packing density of BTA or TTA on the copper metal surface [13,14]. Knowledge about the interaction between TTA and copper metal is important to understand the depletion mechanism of TTA in solution in the presence of free chlorine.

Cuprous oxide ( $Cu_2O$ ) is the dominant form of copper corrosion product in the initial time period (for up to 3 days) of exposure to corrosive water [15–17]. A thin layer of cuprous oxide is formed on copper when air-dried even before exposing a sample to an aqueous system. A previous study [10] showed that BTA forms a corrosion protection layer comprising copper, cuprous oxide, and copper (I)–BTA. It was observed that in the absence of a cuprous oxide layer, corrosion protection efficiency of BTA was reduced by five times [10], suggesting adsorption of BTA on cuprous oxide, though this was not studied in detail.

Free chlorine, commonly used as a biocide in power plant cooling systems, increases copper and copper alloy oxidation rate in cooling systems [14, 18–20]. Several studies have shown that available TTA in solution is reduced significantly when free chlorine is added in solution in the presence of copper metal [13, 14, 21, 22]. Free chlorine can penetrate the protective film and oxidize the underlying copper metal surface directly [21, 22]. In the absence of copper metal and in the presence of free chlorine, about 10% of TTA was found to be depleted from solution [14]. This depletion of TTA was likely due to the formation of chlorotolyltriazole compound, which rapidly switches to original TTA in the absence of free chlorine when free chlorine decomposes to chloride ion [7]. Some hypotheses exist regarding the degradation of TTA protective film on copper alloy surface in the presence of free chlorine [13, 14]. However, the depletion of TTA from solution in the presence of copper metal with varying concentration of free chlorine was not studied.

The specific objectives of this study were to (1) assess the influence of TTA on the anodic and cathodic corrosion behavior of copper in synthetic treated municipal wastewater with varying concentration of free chlorine and evaluate corrosion inhibition efficiency of TTA using electrochemical polarization resistance measurements, (2) study depletion of TTA in solution with increasing oxidation of copper metal caused by free chlorine, (3) assess the adsorption of TTA on cuprous oxide, and (4) investigate influence of pH on the adsorption of TTA on cuprous oxide.

## 2 Materials and Methods

### 2.1 Preparation of Synthetic Cooling Water

A synthetic recipe formulated using MINEQL+ [23] to simulate pH, alkalinity, and total dissolved solids of cooling water was used in the experiments of the present study. The synthetic recipe was prepared to represent four factors of concentration of treated municipal wastewater. The four factors of concentration indicate that total dissolved constituents of the water are four times of that of the makeup water. This concentration denotes a representative degree of concentration, which exists in recirculating cooling water systems. The simplified, synthetic secondary treated municipal wastewater at four factors of concentration was prepared with 1,170 mg/L NaCl (making  $Cl^-$  concentration of 33 mM), 437 mg/L  $NaHCO_3$ , and pH 8.5. The amount of  $NaHCO_3$  was varied to attain other pH values (pH 8.0 and pH 9.0). Ammonia was not considered in the synthetic cooling water recipe, since almost all of the ammonia gets removed through volatilization out of the cooling water in the cooling system [1].

## 2.2 Chemicals Used

A mixture of 4- and 5-methylbenzotriazole was used in the present study as corrosion inhibitor TTA. TTA stock solutions were prepared from a commercial sodium tolyltriazole solution (which contained 50% sodium tolyltriazole, less than 0.5% sodium hydroxide and around 49.5% water by weight) procured from the National Colloid Co. (Steubenville, Ohio). The tolyltriazole solution is miscible and stable in water and has a  $pK_a$  value of 8.42 [24,25].

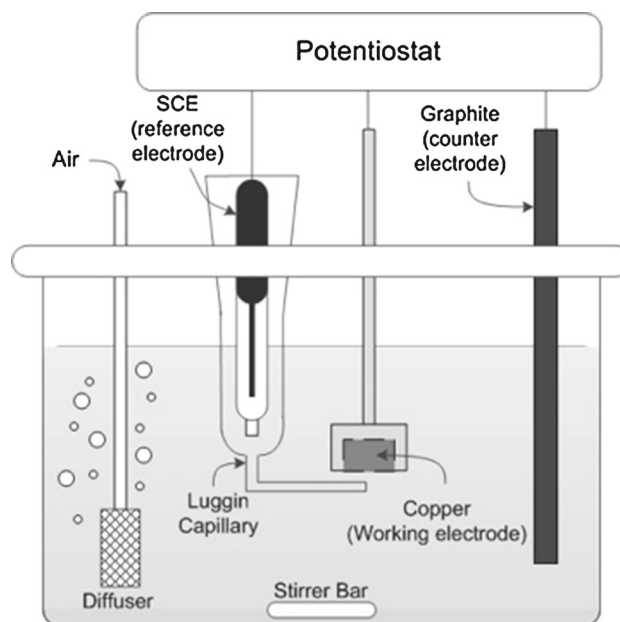
Cuprous oxide used for TTA adsorption analysis was in powdered form (97%  $Cu_2O$ ) and procured from Acros Organics, New Jersey. Surface area of the cuprous oxide particles was measured to be  $1.93\text{ m}^2/\text{g}$  using BET  $N_2$  adsorption technique. Point of zero surface charge ( $pH_{PZC}$ ) of cuprous oxide particles was determined to be 11.6.

## 2.3 Metal Alloy Pre-exposure Treatment

Cylindrical copper metal specimens were used in potentiodynamic polarization and TTA depletion studies. The copper specimens (UNS C10100, Composition:  $Cu \geq 99.99\%$ ) were 0.95 cm in diameter and 1.27 cm in length and were obtained from McMaster-Carr (Cleveland, Ohio). Prior to exposure of the cylindrical metal samples, they were wet-polished with SiC paper to a 600 grit surface finish, dried, degreased with acetone, and rinsed with distilled water. After pre-exposure treatment, the metal samples were immersed into synthetic cooling water.

## 2.4 Corrosion Cell

A corrosion cell of 1L volume was used for electrochemical studies. Figure 2 shows schematic of the glass reactor corrosion cell with the electrodes and their connections to the potentiostat device. A three-electrode system was used to develop polarization curves for copper metal specimens. The copper specimen served as a working electrode, graphite served as a counter electrode, and saturated calomel electrode served as a reference electrode in a Luggin capillary probe. The synthetic cooling water was aerated by purging air into the solution, and temperature of the water was kept at room temperature ( $25 \pm 1^\circ\text{C}$ ). Although the temperature of cooling water in power plants is around  $40^\circ\text{C}$  [1,2], the experiments were carried out at  $25^\circ\text{C}$  in the present study. Elevated temperature has an accelerated influence on copper corrosion [26]. But the effect of elevated temperature on copper corrosion in cooling system was not assessed in this study. The present study focused on the influence of TTA on the corrosion behavior of copper metal in synthetic treated municipal wastewater with varying concentration of free chlorine.



**Fig. 2** Schematic of corrosion cell for electrochemical potentiodynamic studies

## 2.5 Instrumentation

A VersaSTAT3 potentiostat (Princeton Applied Research, Oak Ridge, Tennessee) was used for electrochemical potentiodynamic polarization measurement. High-pressure liquid chromatography (HPLC 1100 Series, Agilent Technology) was used to measure concentration of TTA in the water. The eluent used for HPLC analysis consisted of 49.8% deionized (DI) water, 49.8% methanol, and 0.4% formic acid (volume based). BET surface area of cuprous oxide particles was determined using the BET  $N_2$  adsorption technique (NOVA 2200e Surface Area and Pore Size Analyzer). Electrophoresis analysis of cuprous oxide particles was done to calculate the zeta potential and to identify the pH of point of zero charge (PZC). The electrophoresis analysis was done using a Malvern Zetasizer Nano (Malvern Instruments, Worcestershire, UK).

## 2.6 Potentiodynamic Polarization Study

Potentiodynamic polarization was used to study the anodic and cathodic behavior of copper in the presence of TTA, and varying concentrations of free chlorine. Influence of TTA addition was also evaluated with a control test with no TTA and no free chlorine added to the synthetic cooling water. Different concentrations of free chlorine were used to achieve different biocide dosing scenarios in the synthetic cooling water at pH 8.5. The potentiodynamic polarization study was carried out to observe the change in copper corrosion rate

with increasing free chlorine concentration in the presence of TTA.

Five conditions were tested in the potentiodynamic polarization study with a copper electrode immersed in a 1L corrosion cell filled with cooling water. The conditions tested were as follows: (a) Control (no TTA and no free chlorine), (b) 1 ppm TTA, (c) 1 ppm TTA + 0.5 ppm free chlorine, (d) 1 ppm TTA + 1 ppm free chlorine, and (e) 1 ppm TTA + 3 ppm free chlorine in solution. Although previous studies have indicated higher dosing of TTA for copper corrosion management, for the present study, TTA concentration of 1 ppm has been selected to observe the impact of changing free chlorine concentration in the presence of copper metal on solution TTA concentration.

The potentiodynamic polarization method applies potential over a range relative to the copper electrode (which served as the working electrode) to obtain a polarization curve for copper in a particular aqueous solution. A Tafel plot, illustrating the relationship between potential and current density (taken as absolute value of current in logarithmic scale), can be constructed using the potentiodynamic polarization data. As the applied potential increases, from initial potential value to the stable corrosion potential of the copper metal alloy, the relationship between applied potential and log of current density in the Tafel plot describes cathodic reaction (reduction) of the metal alloy. When potential scan is continuously applied over the stable corrosion potential to the maximum value, the relationship between potential and log of current density in the Tafel plot describes anodic reaction (oxidation) of the metal alloy. An idea on comparative corrosiveness among different aqueous systems can be made through assessment of polarization curves generated from those systems.

The copper specimen acting as a working electrode was embedded in epoxy, resulting in an exposed surface area of  $0.71 \text{ cm}^2$ . In each test, the copper electrode was immersed in the corrosion cell containing 1 ppm TTA and/or free chlorine (or no TTA and no free chlorine—for test condition (a)) for 1 h. After 1 h. of electrode immersion, a potentiodynamic polarization scan was performed. The potentiodynamic scans were performed from  $-300$  to  $+300 \text{ mV}$  versus SCE at a scanning rate of  $0.3 \text{ mV/s}$  [27] to generate the polarization curves.

### 2.7 TTA Depletion Study

To study depletion of TTA from solution, TTA concentration was monitored in synthetic cooling water (at pH 8.5) in the presence of copper metal specimens and different concentrations of free chlorine. Two cylindrical copper metal specimens, having a combined total surface area of  $10.05 \text{ cm}^2$ , were immersed in a 1L reactor with synthetic cooling water for 4 h. The solutions were dosed with 1 ppm TTA and vary-

ing concentrations (0, 0.5, 1, and 3 ppm) of free chlorine. TTA concentration in the solution was monitored at different time intervals by HPLC analysis of water samples.

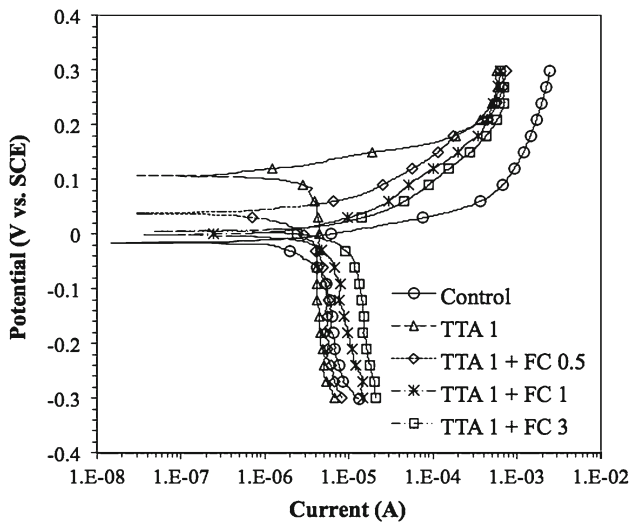
### 2.8 Cuprous Oxide Surface Charge Study

Zeta potential was determined using electrophoresis analysis of a  $20 \text{ mg/L}$  cuprous oxide suspension with background electrolyte concentration of 0.01 and 0.05 M of sodium nitrate ( $\text{NaNO}_3$ ). The cuprous oxide suspension was sonicated for 20 min and then stirred for 1 h to prepare a homogeneous suspension. After that, the pH of the cuprous oxide suspension was adjusted to different values (between pH 6 and 13). A sample from the cuprous oxide suspension was taken for electrophoresis analysis after each suspension pH adjustment. Eight samples were collected at different pH values (between pH 6 and 13) and background electrolyte concentration (0.01 or 0.05 M). Electrophoresis analysis was done using a  $1.0 \text{ mL}$  sample in the Malvern Zetasizer Nano (Malvern Instruments, Worcestershire, UK) instrument. Before each reading, the samples were sonicated for 2 min and shaken well to make a homogeneous suspension of cuprous oxide. The concentration of cuprous oxide was selected to facilitate the electrophoresis analysis. After sonication, the  $20 \text{ mg/L}$  cuprous oxide suspension became homogeneous, and the electrophoretic movement was easily detectable in the instrument to ascertain the surface charge of cuprous oxide.

### 2.9 TTA Adsorption Film Study on Cuprous Oxide

The study of TTA adsorption on cuprous oxide was carried out to quantify the TTA adsorption film density. The adsorption experiments were carried out in reactors having  $0.25 \text{ L}$  synthetic cooling water and  $0.05 \text{ g}$  cuprous oxide in suspension. The cuprous oxide concentration was so selected that the TTA concentration is not entirely adsorbed, and some residual TTA is available in solution. The cuprous oxide provided an adsorption surface area for TTA, and the results were normalized with respect to cuprous oxide surface area for developing adsorption isotherms. TTA concentration was varied from 1 to 50 ppm in the synthetic cooling water. The cuprous oxide suspension was stirred in solution for 24 h. For each test, at the end of 24 h, TTA concentration was measured in the filtered (using  $0.2 \mu\text{m}$  syringe filters) supernatant water. The amount of TTA adsorbed on cuprous oxide surface was measured by subtracting the concentration of TTA present in the solution with cuprous oxide from the original concentration of TTA in solution (without the cuprous oxide). The adsorption study was carried out at pH values of 8.0, 8.5, and 9.0. For the experiment carried out at pH 9.0, TTA concentration in the water was monitored with time.





**Fig. 3** Tafel plots showing results of potentiodynamic polarization experiments with synthetic cooling water at pH 8.5, TTA (1 mg/L), and variable free chlorine concentration (0, 0.5, 1, and 3 ppm)

### 3 Results and Discussion

#### 3.1 Influence of Increasing Free Chlorine on Copper Anodic and Cathodic Corrosion Behavior in the Presence of TTA

The polarization curves generated through potentiodynamic polarization experiments indicate the influence of varying free chlorine concentration on anodic and cathodic corrosion behaviors of copper in the presence of 1 ppm TTA at pH 8.5 (Fig. 3). It was observed that addition of 1 ppm TTA retarded both anodic and cathodic reactions. The anodic reaction (indicated by the potential range higher than the corrosion potential in the Tafel diagram) was significantly retarded compared to the control experiment condition. The polarization resistance curve shifted to the left lowering the corrosion current density and hence the corrosion rate. The corrosion potential increased with the addition of TTA. With increas-

ing free chlorine concentration in the synthetic cooling water, the cathodic reaction (indicated by the potential range lower than the corrosion potential in the Tafel diagram) shifted the polarization curve to the right, and the corrosion potential and the corrosion current density increased compared to the case of using 1 ppm TTA only. The anodic reaction was also increased due to presence of free chlorine, but increasing concentration of free chlorine did not significantly enhance the anodic reaction rate (Fig. 3).

The values of polarization resistances ( $R_p$ , ohm/cm<sup>2</sup>), corrosion potentials ( $V$ ), corrosion current densities (A/cm<sup>2</sup>), corrosion rates (mm/year), and corrosion inhibition efficiencies have been determined according to the ASTM G59 [28] and given in Table 1. The corrosion inhibition efficiencies have been determined for the scenarios where corrosion inhibitor TTA and free chlorine were used, in comparison with the control scenario. The value of the Stern and Geary constant (mentioned in ASTM G59 [28]) for copper metal alloy was obtained from the modified Stern and Geary constant provided in Choudhury et al. [29]. The corrosion inhibition efficiency values in Table 1 show that increasing concentrations of free chlorine in the presence of TTA caused an increase in the copper corrosion rate in synthetic cooling water.

#### 3.2 Analysis of TTA Depletion in the Presence of Copper and Free Chlorine

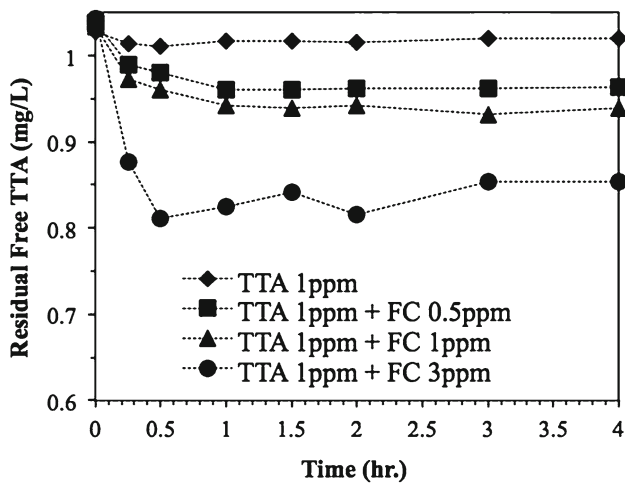
The TTA depletion profile in synthetic cooling water (pH 8.5), with varying concentration of free chlorine, is shown in Fig. 4. From Fig. 4, it may be seen that increasing copper corrosion rate was accompanied by more loss of TTA from solution.

Hsieh et al. [14] proposed a hypothesis regarding degradation of TTA by free chlorine in the presence of copper metal based on a mass balance analysis for TTA. Experimental results showed that in the absence of free chlorine, the sum of the TTA adsorbed on the copper surface and present in solution was equal to the amount of dosed TTA in solution

**Table 1** Influence of increasing free chlorine concentration on copper corrosion in the presence of corrosion inhibitor TTA

Experimental scenario	Polarization resistance $R_p = \Delta E / \Delta I$ (ohm/cm <sup>2</sup> )	Corrosion potential versus SCE (V)	Corrosion current density (A/cm <sup>2</sup> )	Corrosion rate (mm/year)	Corrosion inhibition efficiency (%)
Control	5,545	-0.015	10.54	0.25	-
TTA 1 ppm	14,539	0.107	4.02	0.09	61.9
TTA 1 ppm + free chlorine 0.5 ppm	9,156	0.038	6.38	0.15	39.4
TTA 1 ppm + free chlorine 1 ppm	6,330	-0.002	9.24	0.22	12.4
TTA 1 ppm + free chlorine 3 ppm	3,143	0.005	18.60	0.43	-76.4

The polarization resistance, corrosion potential, corrosion current density, and corrosion rate values have been calculated from the potentiodynamic polarization study following ASTM G59. Corrosion inhibition efficiencies have been determined in comparison to the control scenario  
TTA tolyltriazone, SCE saturated calomel electrode

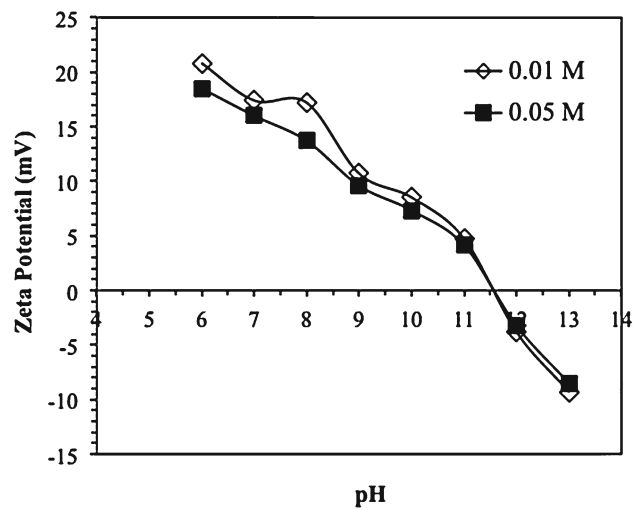


**Fig. 4** TTA depletion (initial concentration ~1 ppm) in synthetic cooling water under different concentrations of free chlorine (0, 0.5, 1, and 3 ppm) in the presence of copper metal

after two hours [14]. In the presence of free chlorine, the sum of TTA on the copper surface and present in solution was about 70 % less than the initially dosed TTA in solution after two hours [14]. Based on these results, it was hypothesized that the presence of copper metal had a catalytic effect in the degradation of TTA by free chlorine [14]. In the absence of copper metal and in the presence of free chlorine, TTA concentration was lowered by about 10 %, likely through formation of chlorotolyltriazole, which converts back to TTA in the absence of free chlorine [7, 14]. However, similar mass balance studies of TTA adsorption on copper metal surface by Lu et al. [13] showed that even in the absence of free chlorine, the sum of TTA on copper surface and TTA in solution was less than the initially dosed TTA in solution for experiments carried out for longer time duration (3 h or more). The HPLC analysis carried out in the present study did not observe any peak for chlorotolyltriazole. Hence, the hypothesis of TTA degradation by free chlorine in the presence of copper metal is not well supported by mass balance analysis of TTA on copper surface and in solution. The loss of TTA from solution may be attributed to more adsorption of TTA on to the cuprous oxide surface formed with enhanced corrosion of copper metal and to the formation of insoluble copper–TTA complex with the released copper ions in solution.

### 3.3 $pH_{PZC}$ Analysis of Cuprous Oxide

The results from the electrophoresis analysis were used to determine the point of zero charge (PZC) pH value of  $Cu_2O$  (s) in water. The  $pH_{PZC}$  value of the cuprous oxide particles used in this study was 11.6, which is close to 11.5, the  $pH_{PZC}$  of cuprous oxide reported in the literature [10]. Figure 5 shows the zeta potential versus pH curves of the cuprous

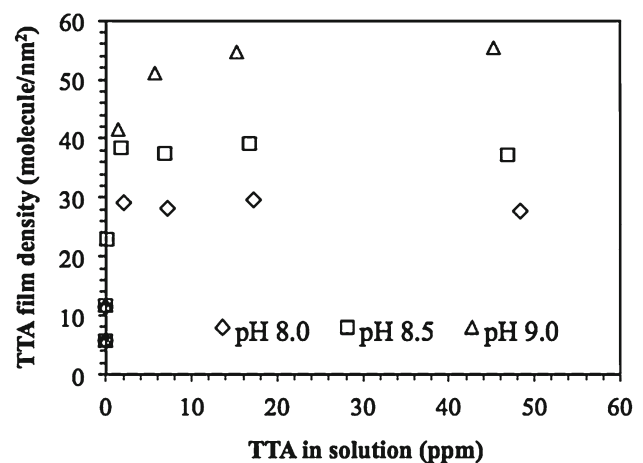


**Fig. 5** Zeta potential versus pH curves for cuprous oxide powder in aqueous suspension at background electrolyte ( $NaNO_3$ ) concentrations of 0.01 and 0.05 M

oxide powders used in the present study at background electrolyte concentration of 0.01 and 0.05 M.

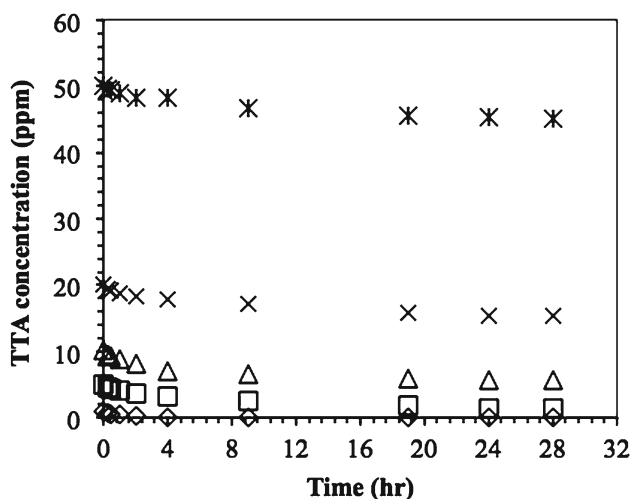
### 3.4 Analysis of TTA Adsorption Film on Cuprous Oxide

TTA adsorption isotherms on cuprous oxide surface in synthetic cooling water at pH values of 8.0, 8.5, and 9.0 are shown in Fig. 6. For the adsorption experiment carried out at pH 9.0, water samples were collected from the synthetic cooling water at different times to measure TTA concentration in solution. Figure 7 shows the TTA depletion kinetics in synthetic water at pH 9.0. From Fig. 7, it can be seen that



**Fig. 6** TTA adsorption isotherms for adsorption on cuprous oxide ( $Cu_2O$ ) in synthetic cooling water at different pH values (8.0, 8.5, and 9.0). Total cuprous oxide concentration,  $(Cu_2O)_T = 0.2$  g/L. Data acquired after 24 h. contact period (equilibrium reached after 24 h contact time)





**Fig. 7** TTA depletion kinetics in synthetic cooling water (pH 9.0) with 0.2 g/L cuprous oxide for experiments having initial TTA concentration of 1–50 ppm. *Legends, diamond 1 ppm, square 5 ppm, triangle 10 ppm, times symbol 20 ppm, cyrillic small letter zhe 50 ppm*

TTA concentration gradually decreased and reached a relatively lower and stable value after 24 h of immersion. Hence, equilibrium can be assumed for TTA adsorption on cuprous oxide after 24 h.

The calculated adsorption film density was dependent on the pH of the solution. Projection area of Cu(I)–TTA complex is calculated to be about 0.22–0.50 nm<sup>2</sup> (calculated using MarvinSketch 5.9.4, ChemAxon Ltd). Surface area of cuprous oxide particles used in this study was determined to be 1.93 m<sup>2</sup>/g from BET analysis. From the maximum adsorbed TTA concentration in the pH range of 8–9, the TTA polymeric film on cuprous oxide can be estimated as being about 6.8–27.8 layers. With the projection radius of the Cu(I)–TTA molecule as 0.26–0.40 nm, the film thickness can be estimated to be 3.5–22.1 nm.

The observed TTA polymeric film thickness on cuprous oxide surface is higher than that on copper metal surface (3.6–9.4 nm) reported in previous study [14]. Even at pH 8.0, the adsorption film density of TTA on cuprous oxide (30 molecule/nm<sup>2</sup>) was higher than the adsorption film density of TTA on copper metal (20–25 molecule/nm<sup>2</sup>), determined at pH 8.8 in a previous study by Hsieh et al. [14]. This result is similar to that obtained from previous studies, which showed BTA (a compound similar to TTA) adsorbed more rapidly on cuprous oxide surface compared to copper metal surface and formed a thicker layer of adsorbate [9,30,31].

The adsorption isotherm data given in Fig. 6 were not consistent with monolayer site binding. Adsorbed film thickness calculation using projected area of Cu(I)–TTA complex and the total surface area (1.93 m<sup>2</sup>/g) of adsorbent indicated that TTA adsorption on cuprous oxide surface occurred through multilayer binding.

Previous investigators have reported that the first layer of BTA (a compound similar to TTA) on copper or copper oxide surface is a layer of de-protonated BTA (BTA<sup>-</sup>) adsorbed by coordination bonding to the copper on the surface [30,32]. For subsequent layers of adsorption, at least one of the triazole nitrogen in the initially adsorbed BTA<sup>-</sup> molecule should remain free and available for coordination with released cuprous ions, which bind with the adsorbed BTA<sup>-</sup> molecule and then serve as a bridging metal for chain growth [9]. Based on the knowledge of BTA<sup>-</sup> interaction with Cu<sub>2</sub>O and copper surfaces, it can be hypothesized that de-protonated TTA (TTA<sup>-</sup>) forms complex with copper on the cuprous oxide surface.

### 3.5 Free Energy of Adsorption for TTA on Cuprous Oxide Surface

Using the conventional diprotic acid model for hydrous metal oxide surfaces [33], the surface hydroxyl species on the hydrated Cu<sub>2</sub>O surface can be represented as ≡CuOH<sub>2</sub><sup>+</sup>, ≡CuOH<sup>0</sup>, and ≡CuO<sup>-</sup>. As pH<sub>PZC</sub> of cuprous oxide is 11.6, in the pH range of 8–9, the dominant surface hydroxyl species can be represented by ≡CuOH<sub>2</sub><sup>+</sup>. At pH range of 8–9, de-protonated TTA (TTA<sup>-</sup>) present in solution will be adsorbed on the cuprous oxide layer by forming surface complexes with hydroxyl species ≡CuOH<sub>2</sub><sup>+</sup>. The adsorbed TTA<sup>-</sup> concentrations from surface film density analysis study were used to prepare Langmuir adsorption isotherms, as the Langmuir isotherms were found to fit the adsorption data well. The free energy of adsorption (ΔG<sup>o</sup><sub>ads</sub>) can be used as an indicator to determine whether the adsorption is physisorption (if ΔG<sup>o</sup><sub>ads</sub> is less negative than -20 kJ/mol) or chemisorption (if ΔG<sup>o</sup><sub>ads</sub> is close to -40 kJ/mol or more negative) [34]. The TTA adsorption reaction on cuprous oxide can be given as;

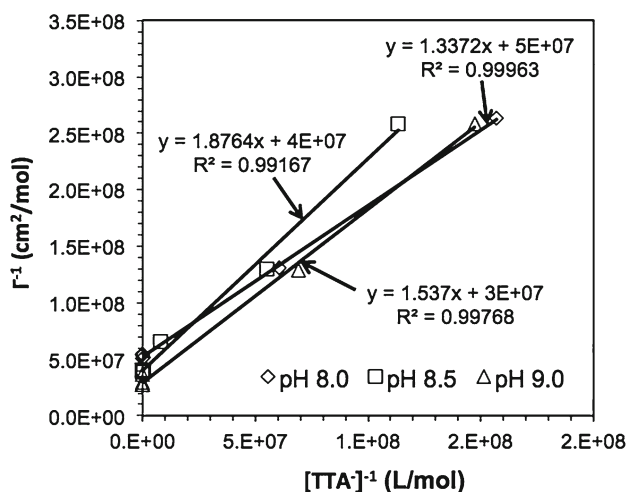


The adsorption equilibrium constant K<sub>ads</sub> (L/mol) in the dilute aqueous solution can be expressed as,

$$K_{\text{ads}} = \frac{[\equiv\text{CuOH}_2\text{TTA}]}{[\text{TTA}^-] \cdot [\equiv\text{CuOH}_2^+]} \quad (2)$$

where [TTA<sup>-</sup>] is the total de-protonated tolyltriazole concentration in solution (mol/L), Γ = [≡CuOH<sub>2</sub>TTA] is the concentration of cuprous oxide–TTA surface complexes (mol/cm<sup>2</sup>), and [≡CuOH<sub>2</sub><sup>+</sup>] is the surface concentration of free (unoccupied) adsorption sites (mol/cm<sup>2</sup>). With [≡CuOH<sub>2</sub>TTA] expressed as Γ and the maximum surface site concentration expressed as Γ<sub>max</sub> (= [≡CuOH<sub>2</sub>TTA] + [≡CuOH<sub>2</sub><sup>+</sup>]), Eq. 2 can be re-arranged in the following form:

$$\Gamma^{-1} = \Gamma_{\text{max}}^{-1} + \Gamma_{\text{max}}^{-1} K_{\text{ads}}^{-1} [\text{TTA}^-]^{-1} \quad (3)$$



**Fig. 8** Plot of  $\Gamma^{-1}$  versus  $[\text{TTA}^{-}]^{-1}$  for adsorption of de-protonated tolyltriazole ( $\text{TTA}^{-}$ ) on  $\text{Cu}_2\text{O}$  in synthetic cooling water at three pH values (8.0, 8.5, and 9.0). The linear relationship indicates the adsorption of  $\text{TTA}^{-}$  on cuprous oxide is a Langmuir type. Where  $\Gamma$  indicates the cuprous oxide–TTA surface complexes [ $\equiv \text{CuOH}_2\text{TTA}$ ], and  $[\text{TTA}^{-}]$  indicates the free  $\text{TTA}^{-}$  solution concentration in equilibrium with solid cuprous oxide

A plot of  $\Gamma^{-1}$  versus  $[\text{TTA}^{-}]^{-1}$  gives values of an intercept ( $\Gamma_{\text{max}}^{-1}$ ) and slope ( $\Gamma_{\text{max}}^{-1} K_{\text{ads}}^{-1}$ ) that is related to Langmuir adsorption isotherm parameters. The adsorption experiment data were used to obtain  $\Gamma^{-1}$  versus  $[\text{TTA}^{-}]^{-1}$  plot as shown in Fig. 8. The plots for different pH values were used to determine respective  $\Gamma_{\text{max}}$  and  $K_{\text{ads}}$  values. The free energy of adsorption was then calculated through the following equation:

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln K_{\text{ads}} \quad (4)$$

where  $R$  is the gas constant (8.314 J/mol.K) and  $T$  is the absolute temperature (298 K). The calculated  $\Delta G_{\text{ads}}^{\circ}$  values at different pH values are indicated in Table 2, which is in the range of values typical of chemisorption reactions.

The adsorption data showed that maximum TTA was adsorbed at pH 9.0. Assuming maximum surface site concentration ( $\Gamma_{\text{max}}$ ) of cuprous oxide to be the maximum TTA adsorbed at pH 9.0, we get  $\Gamma_{\text{max}} = 3.55 \times 10^{-5}$  mol/L. Using this value of  $\Gamma_{\text{max}}$ , surface site density of cuprous oxide was calculated to be 9.78 sites/nm<sup>2</sup>. Which is comparable to the site density of other metal oxides like hydrous ferric oxide (2.31 sites/nm<sup>2</sup>), Geothite

**Table 2**  $\Delta G_{\text{ads}}^{\circ}$  values at different pH for TTA adsorption on cuprous oxide

pH	$\Delta G_{\text{ads}}^{\circ}$
8.0	−43.31
8.5	−41.81
9.0	−41.53

(2 sites/nm<sup>2</sup>),  $\alpha$ –FeOOH(10 sites/nm<sup>2</sup>),  $\alpha$ –Al<sub>2</sub>O<sub>3</sub>(10 sites/nm<sup>2</sup>), TiO<sub>2</sub>(10 sites/nm<sup>2</sup>), and Gibbsite (8.0–8.8 sites/nm<sup>2</sup>) [35].

#### 4 Summary and Conclusions

Findings in this study contribute to the understanding of corrosion inhibition of copper metal by TTA in the presence of free chlorine. More depletion of TTA was observed from solution with increasing free chlorine dosing in the presence of copper metal. This may be attributed to more adsorption of TTA on to the cuprous oxide surface formed with enhanced corrosion of copper metal and to the formation of insoluble copper–TTA complex with the released copper ions in solution. So in order to determine the TTA dosing in a cooling system, using treated municipal wastewater as makeup water, adequate dosing of TTA should be taken into account considering depletion of TTA in the presence of free chlorine as biocide.

The study showed that TTA adsorbs more onto cuprous oxide than on copper metal surface, corroborating similar findings with BTA in previous studies. The film density of TTA on the cuprous oxide surface was pH dependent. For a similar pH range (pH 8–9), the packing density of TTA adsorbed onto cuprous oxide (30 molecules/nm<sup>2</sup>) was more than the packing density of TTA onto copper metal (20–25 molecules/nm<sup>2</sup>). The pH 8–9 range used in the study was representative of the usual pH range observed in cooling systems using treated municipal wastewater as makeup water [1].

TTA film density on cuprous oxide surface increased with increasing pH. With increasing pH concentration of de-protonated,  $\text{TTA}^{-}$  increases in solution. As a result, more  $\text{TTA}^{-}$  can coordinate to cuprous oxide surface and subsequent adsorbed layers.

The electrochemical potentiodynamic polarization measurements in synthetic cooling water demonstrated that increasing free chlorine concentration enhanced copper corrosion. Thus, more cuprous oxide corrosion product was formed on copper metal surface at higher concentrations of free chlorine. This caused more TTA to deplete from the solution through adsorption on cuprous oxide and through formation of insoluble copper–TTA complexes with released copper ions, when free chlorine and copper metal were simultaneously present.

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