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Effect of Tolyltriazole on the Corrosion Protection of Copper against Ammonia and Disinfectants in Cooling Systems

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Tolyltriazole (TTA) has been widely used as a corrosion inhibitor for copper and copper alloy heat exchanger components in power plant cooling water systems. In this work the effectiveness of TTA protection in the presence of free chlorine, monochloramine, and ammonia was studied, in the context of using secondary treated municipal wastewater as cooling water. Results indicated that the corrosiveness of ammonia becomes negligible in the presence of TTA. Also, monochloramine represents a better disinfection agent in terms of copper corrosion protection by TTA than free chlorine. The packing density, film thickness, and number of layers of TTA adsorbed on the Cu surface were estimated from measurements and compared with estimates from other studies. It was found that copper can work as a catalyst for free chlorine to degrade TTA and that the surface packing density, film thickness, and number of layers increased in the presence of monochloramine.

1. Introduction

Control of corrosion of copper and copper alloy heat exchanger components in power plant cooling water systems is important and also technically challenging, especially when the quality of water used in the cooling system is low. The lower quality of secondary treated municipal wastewater relative to freshwater makes its reuse in power plant cooling water systems difficult due to copper corrosion caused by ammonia and biocide, among other issues.

Tolyltriazole (TTA) and benzotriazole (BTA) have been widely used as corrosion inhibitors for copper and copper alloys,[1−3] including in cooling water systems.[4,5] TTA is a derivative of BTA with a methyl group substituted in the benzene ring. Thus, TTA could be 4- or 5-methylbenzotriazole.[4] The substitution of a methyl group in the benzene ring makes TTA more effective in corrosion control of copper and copper alloys, due to the hydrophobic character of the methyl group.[4,6]

BTA and TTA function in corrosion inhibition by forming a protective polymeric film, Cu(I)-BTA or Cu(I)-TTA, on the copper or copper alloy surface.[6−8] The formation of the protective polymeric film is via the chemisorption of BTA or TTA onto the copper or copper alloy surface, involving the complexation of surface copper atoms and the triazole group of BTA or TTA molecules.[6,9] The chemisorbed triazole group bonds to copper atoms through lone-pair electrons of the nitrogen atoms.[10] The thickness of single polymeric layers of BTA and 4-methylbenzotriazole are approximately 3 nm, and that of 5-methylbenzotriazole is approximately 7 nm.[6] Although there have been studies proposing the specific orientation of BTA or TTA molecules in the absorbed layer,[3,6,10,11] there is no consensus about the surface structural configuration. There is an agreement that the molar ratio of BTA or TTA to Cu in the adsorption layer is 1:1.[4,6,10,12] Although several experimental techniques have been used to analyze the property of the polymeric film, direct quantitative measurement of the BTA or TTA surface packing density on copper is limited.[13] The direct

measurement of the BTA or TTA surface packing density is desirable since such measurements could enable more accurate estimates of the thickness and number of layers and also be utilized to study the impact of other agents, such as disinfectants, on the Cu(I)-TTA adsorption film.

Ammonia in secondary treated municipal wastewater is a concern with respect to corrosion when reusing the wastewater in power plant cooling water systems. Ammonia has been recognized to be able to complex with copper and cause severe corrosion of copper and copper alloys.[14,15] Although ammonia may be partially or even largely removed by air stripping in cooling tower systems, the removal of ammonia in cooling systems operated under particular conditions is difficult to predict. It has been suggested that the presence of ammonia in a cooling water system requires the addition of BTA for copper corrosion protection against ammonia.[16] However, studies of the influence of ammonia on copper, and BTA or TTA protection of copper against ammonia, have not yet been conducted.

Free chlorine is commonly used for biomass growth control in power plant cooling water systems. However, it has been reported that free chlorine increases the corrosion rate of several metals and metal alloys of interest in cooling systems.[17−19] Also, several studies have shown that the protective film of BTA or TTA on copper is vulnerable to free chlorine.[13,20,21] It has been suggested that free chlorine can penetrate the film and attack copper directly[20,21] or that free chlorine might degrade the protective film.[4] However, neither the mechanisms of how free chlorine might degrade the TTA protective film nor the TTA degradation pathway are clear. When using secondary treated municipal wastewater as power plant cooling water makeup, free chlorine may not be a good choice as biomass control agent since it reacts with organic matter and its disinfection power is reduced.[22,23]

Monochloramine, in contrast, is a promising biomass control agent for use in cooling systems when secondary treated municipal wastewater is used as makeup water. Monochloramine was found to be more effective than or effective similarly to free chlorine against biofilms in cooling water systems.[24,25] Pilot-scale cooling tower tests with secondary treated wastewater showed that monochloramine was an effective biocide.[26] With

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respect to corrosion, several studies have shown that monochloramine is less corrosive than free chlorine to several metals and metal alloys in drinking water distribution systems.[27] However, its influence on copper corrosion and the ability of tolyltriazole to maintain a protective film on copper have not been studied. Monochloramine is an oxidizing agent but with lower oxidation potential than free chlorine,[28] and thus its influence on copper and copper alloys might be similar to free chlorine but less aggressive. An investigation of the mechanisms of the interinfluence among TTA, monochloramine, or free chlorine, and copper is needed for development of effective corrosion control in cooling systems using secondary treated municipal wastewater as makeup water.

The objective of this study was to compare and evaluate the effectiveness of TTA for corrosion protection of copper in cooling systems when secondary treated municipal wastewater is used as makeup water and free chlorine or monochloramine are employed as a biomass control agent. The specific goals of the study were to (1) investigate the anodic and cathodic influence of TTA, ammonia, monochloramine, and free chlorine on copper corrosion, (2) compare the effectiveness of TTA protection against corrosion of copper by ammonia, monochloramine, and free chlorine, and (3) study the depletion of TTA in solution caused by the presence of copper, ammonia, monochloramine, and free chlorine.

2. Experimental Section

2.1. Synthetic Cooling Water and TTA. Synthetic cooling water was prepared to simulate pH, alkalinity, and the total dissolved solids of cooling water consisting of secondary treated municipal wastewater at four cycles of concentration. The synthetic cooling water was prepared with 1170 ppm NaCl, 504 ppm NaHCO$_3$, and pH 8.8.

TTA tested in this study was a mixture of 4- and 5-methylbenzotriazole 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) from the National Colloid Co. (Steubenville, OH). The 50% aqueous solution of sodium tolyltriazole is miscible with and stable in water.[29] TTA has a pK_a value of 8.42, and thus in this study the TTA is predominantly (71%) ionized.[30]

2.2. Metal Alloy Preexposure Treatment. The copper specimens (UNS C10100) tested were cylinder-shaped, 0.95 cm in diameter, and 0.5 or 10 cm in length and were obtained from McMaster-Carr (Cleveland, OH). Prior to being exposed to synthetic cooling water, they were wet-polished with SiC paper to a 600 grit surface finish (to a 2400 grit surface finish for the TTA adsorption film study), dried, degreased with acetone, rinsed in distilled water, and then immersed into synthetic cooling water.

2.3. Corrosion Cells. The corrosion cells used for electrochemical studies were glass reactors with a volume of 1 or 2 L, as shown in Figure 1. A three-electrode system was employed with the copper specimen as a working electrode, graphite as a counter electrode, and saturated calomel electrode as a reference electrode in a Luggin capillary probe. The synthetic cooling water was aerated by purging air into the solution. The temperature of the water was kept at room temperature (25 ± 1 °C).

2.4. Instrumentation. A PGSTAT100 potentiostat (ECO CHEMIE, Utrecht, The Netherlands) was used for electrochemical potentiodynamic polarization and polarization resistance measurements. High-pressure liquid chromatography (HPLC 1100 Series, Agilent Technologies) was used for TTA concen-
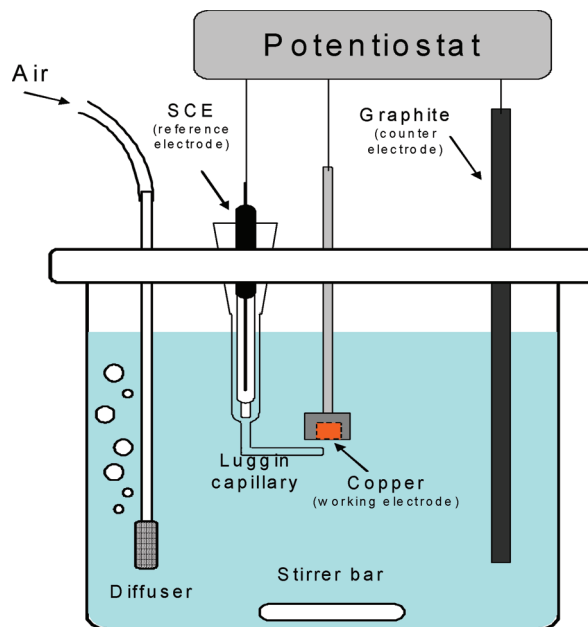

Figure 1. Schematics of the corrosion cell for electrochemical potentiodynamic polarization and polarization resistant studies.

tration analysis, with an eluent of 49.8% DI water, 49.8% methanol, and 0.4% formic acid (volume-based). Calibration curves for different levels of TTA concentration analysis using HPLC were established with R^2 of above 0.995. All the reported TTA concentrations in this study were in the calibration range. The HPLC instrument detection limit of TTA was 1 ppb.

2.5. Potentiodynamic Polarization Study. Potentiodynamic polarization was conducted to study the anodic and cathodic behaviors of copper in the presence of TTA, ammonia, free chlorine, and monochloramine. This method applies potential dynamically over a wide range relative to the copper electrode to acquire a polarization curve (potential vs current) of the copper electrode in a particular aqueous system. The positive-potential (positive potential relative to the open-circuit potential of the copper electrode) part of the polarization curve gives information about the anodic reaction (oxidation) of the copper electrode. The negative-potential part gives information about the cathodic reaction (reduction) of the copper electrode. By comparing the polarization curves derived from a similar aqueous system with a particular parameter varied, the influence of the parameter on corrosion potential, corrosion current density, anodic reaction, and cathodic reaction can be determined. The potentiodynamic polarization curve is usually expressed as a Tafel plot, which is the relationship between potential and current where current is expressed as absolute value in logarithmic scale.

Sixteen conditions were tested in the potentiodynamic polarization study with a copper electrode, as shown in Table 1. A 1 L volume corrosion cell was used to contain the synthetic cooling water. A copper specimen acting as a working electrode was embedded in epoxy giving an exposure surface area of 0.71 cm^2.

In each test, the copper electrode was immersed in the corrosion cell containing synthetic cooling water with or without TTA addition. At 1 h after the electrode immersion, potentiodynamic polarization was performed immediately after the addition of free chlorine, monochloramine, ammonia, or none of the above. A potentiodynamic polarization scan was performed from −250 to +250 mV vs SCE at a scan rate of 0.3 mV/s.

Table 1. Corrosion Potential, Corrosion Current Density, and Inhibition Efficiency after 1 h Exposure Determined from Potentiodynamic Polarization Studies with Copper in Synthetic Cooling Water[a]

test conditions[b]	corrosion potential vs SCE (V)	corrosion current density (A/cm^2)	ratio of corrosion current density compared to that of control	inhibition efficiency[c] (%)
control	−0.049	5.00×10^{-7}		
TTA0.2	−0.092	2.87×10^{-7}	0.574	42.6
TTA1	−0.108	2.30×10^{-7}	0.460	54.0
TTA5	−0.108	1.56×10^{-7}	0.312	68.8
TTA20	−0.094	1.25×10^{-7}	0.250	75.0
FC1	0.008	5.58×10^{-6}	11.2	−1016
FC3	0.048	1.36×10^{-5}	27.2	−2620
FC10	0.073	6.41×10^{-5}	128	−12720
MCA1	0.011	4.23×10^{-6}	8.47	−746
MCA3	0.041	8.47×10^{-6}	16.9	−1590
MCA10	0.055	3.03×10^{-5}	60.7	−33003
NH$_3$-2.8	−0.076	5.28×10^{-7}	1.06	−5.6
NH$_3$-8.4	−0.090	7.80×10^{-7}	1.56	−56
FC1_TTA1	−0.007	5.28×10^{-7}	1.06	−5.6
MCA3_TTA1	−0.006	4.86×10^{-7}	0.973	2.8
NH$_3$-8.4_TTA1	−0.117	1.84×10^{-7}	0.368	63.2

[a] A negative value of inhibition efficiency implies the corrosion was enhanced rather than inhibited. [b] TTAa, tolyltriazole with a ppm; FCb, free chlorine with b ppm as Cl$_2$; MCAc, monochloramine with c ppm as Cl$_2$; NH$_3$-d, ammonia with d ppm as N. Control: synthetic cooling water with no addition of TTA and aggressive constituents. [c] After 1 h exposure.

2.6. Polarization Resistance Study. Polarization resistance was conducted to study the corrosion resistance of copper in the synthetic cooling water in the presence of TTA, free chlorine, monochloramine, and ammonia. The polarization resistance method can be used to determine, semicontinuously, the instantaneous corrosion rate of the electrode.[13] The method involves applying a very small range of potential to a working electrode. Unlike the potentiodynamic polarization method which employs a wide range of potential, the small applied potential of the polarization resistance method does not change the surface properties of the electrode, making semicontinuous monitoring possible. Polarization resistance is defined as the slope of the polarization curve at open-circuit potential. It is inversely proportional to instantaneous corrosion rate. The proportionality factor can be determined by combining the polarization resistance method and the gravimetric weight loss method.[31]

Eight conditions similar to those listed in Table 1 were tested in this study. A 2 L corrosion cell was used to contain the synthetic cooling water. A copper specimen with exposure surface area of 24.7 cm^2 was used.

In each test, polarization resistance measurement was performed semicontinuously for 2 days. All chemicals added were maintained at target concentration levels. Polarization resistance scans were performed from −30 to +30 mV with respect to the corrosion potential at a scan rate of 0.3 mV/s.

2.7. TTA Depletion Study. The depletion of TTA in the synthetic cooling water caused by the presence of copper specimens, free chlorine, monochloramine, or ammonia was studied. Eight copper specimens (each with surface area of 24.7 cm^2) were immersed for 10 h in a 2 L reactor with synthetic cooling water in each test with the addition of TTA 1 ppm. Free chlorine 1 ppm as Cl$_2$, monochloramine 3 ppm as Cl$_2$, ammonia 28 ppm as N, or none of these aggressive species was then added and maintained 1 h after copper specimen immersion. Change of TTA concentration with time in the solution was monitored using HPLC analysis of samples acquired at various times.

2.8. TTA Adsorption Film Study. This study was designed to analyze quantitatively the TTA adsorption film on copper. A reactor with 0.125 L synthetic cooling water was prepared for each test, as shown in Figure 2. There were two parts in this study.
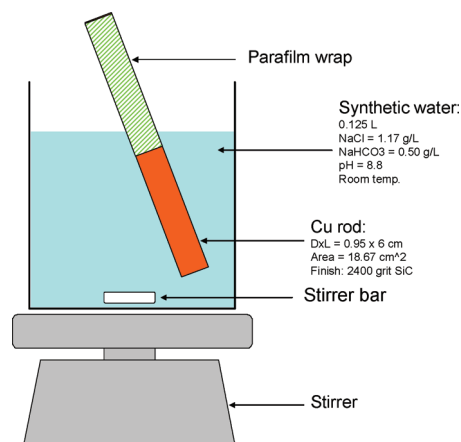
Figure 2. Schematics of the batch reactor for TTA adsorption film study.

In the first part, six conditions were examined. The conditions were the combination of the presence of copper specimens (no copper or copper with exposure area of 18.6 cm^2) and the presence of biocide (no biocide, free chlorine 3 ppm as Cl$_2$, or monochloramine 3 ppm as Cl$_2$). In each condition, 0.025 mg of TTA (total TTA concentration of 0.2 ppm) was added and stirred for 2 h. TTA mass in the solution was then determined by measuring the TTA concentration in the synthetic cooling water by HPLC. If a copper specimen was immersed, it was then removed and immersed in 3.5 mL of 12 N HCl in a glass tube for 5 min for TTA film extraction, a modified acid stripping method.[13] The TTA mass on the copper specimen was then determined by measuring the TTA concentration in the extraction solution by HPLC.

In the second part, synthetic cooling water with TTA concentration ranging from 0.02 to 20 ppm was prepared in the 0.125 L reactor. The water was stirred with the copper specimen immersed for 20 h. For the water with initial TTA concentration ranging from 0.02 to 0.2 ppm, TTA concentration in the water was monitored with time. For each test, at the end of the 20th hour, the TTA concentration in the synthetic cooling water was measured. Also, TTA mass on the copper specimen was determined by the modified acid stripping method described above.
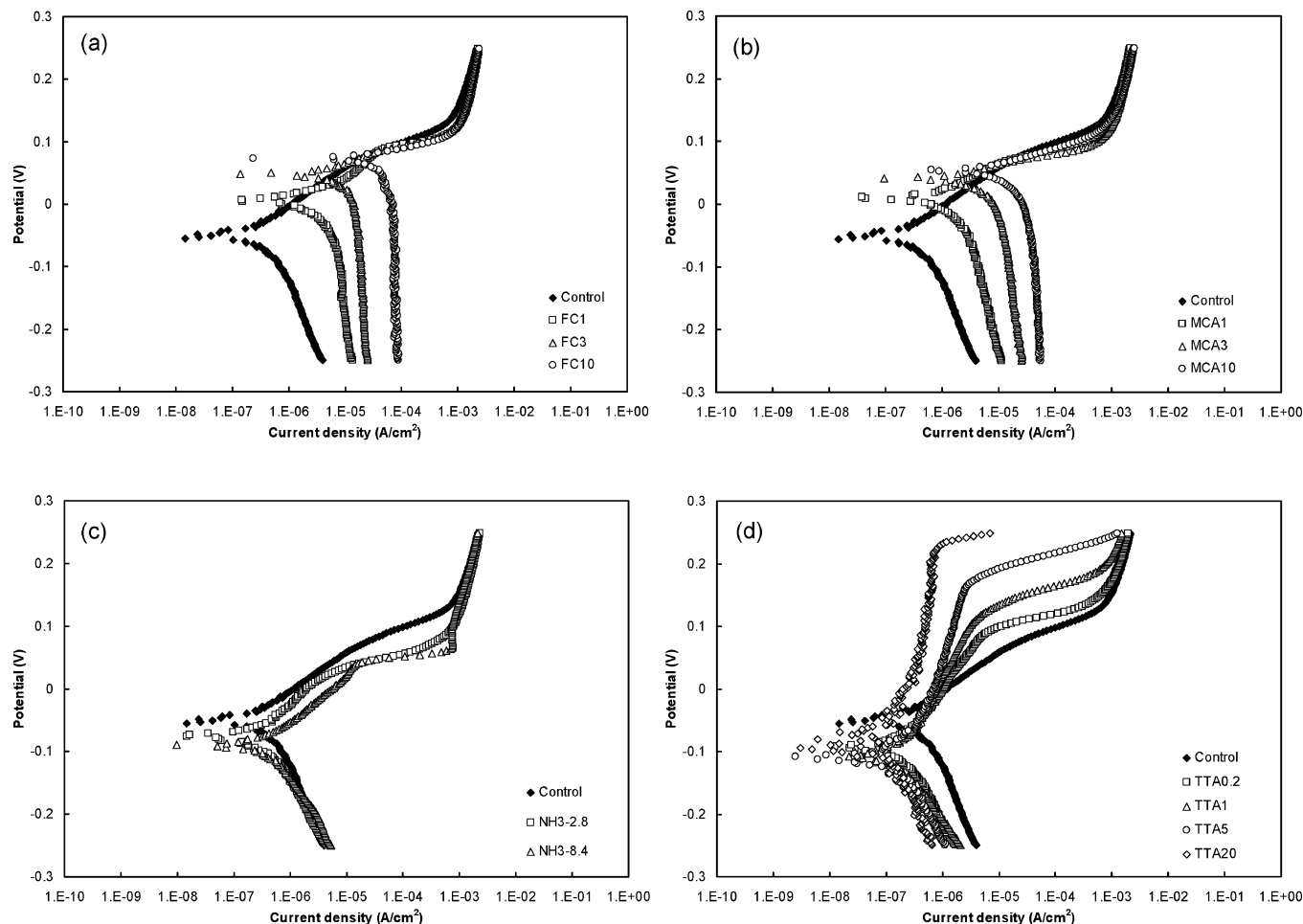
Figure 3. Results of potentiodynamic polarization tests with solutions of (a) free chlorine (FC) 1−10 ppm as Cl_2, (b) monochloramine (MCA) 1−10 ppm as Cl_2, (c) ammonia (NH_3) 2.8 and 8.4 ppm as N, and (d) TTA 0.2−20 ppm. FC and MCA enhanced the cathodic reaction in the copper corrosion process in synthetic water, while ammonia enhanced the anodic reaction (where, for example, 1E-10 represents 1×10^{-10}). TTA retards both cathodic and anodic reactions.

3. Results and Discussion

3.1. Potentiodynamic Polarization Study: Influences of TTA, Free Chlorine, Monochloramine, and Ammonia on Copper Anodic and Cathodic Corrosion Behaviors. The results of the potentiodynamic polarization studies of the effects of TTA, free chlorine, monochloramine, and ammonia on copper anodic and cathodic corrosion behaviors are shown in Figure 3. Table 1 shows the results of corrosion potentials, corrosion current densities, and corrosion inhibition efficiency after 1 h exposure determined from potentiodynamic polarization studies with copper in synthetic cooling water.

Figure 3a indicates that free chlorine enhanced the cathodic reaction of the polarization curve. The cathodic reaction shifted the polarization curve to the right, and the corrosion potential and the corrosion current density increased (Table 1). Also, the higher the concentration of free chlorine, the more the curve was shifted to the right. The anodic part of the polarization curve was not influenced. The cathodic reaction of metal and metal alloys in an aerated aqueous solution is dominated by hydrogen reduction enhanced by oxygen, which acts as a depolarizer and accelerates the cathodic reaction by preventing the accumulation of hydrogen ions on the metal or metal alloy surface.[1] Free chlorine might also work as a depolarizer which enhances the hydrogen reduction reaction. In the absence of a depolarizer, the hydrogen reduction reaction has two steps: (1) the adsorption of hydrogen ion onto the metal surface and (2) the combination of two neutral-charged hydrogen atoms to form hydrogen gas.[15]

The second step is the rate-determining step, and the accumulation of hydrogen atoms on the metal surface is usually the key factor in the polarization of the cathodic reaction. We hypothesize that free chlorine directly removes hydrogen atoms from the copper surface, which prevents their accumulation, thus mitigating the cathodic polarization and enhancing the corrosion rate.

Figure 3b, similar to Figure 3a, indicates that monochloramine enhanced the cathodic reaction of the polarization curve. Correspondingly, the corrosion potential and the corrosion current density both increased (Table 1). We hypothesize that monochloramine also works as a depolarizer to prevent the accumulation of hydrogen atoms on the copper surface, thus enhancing the overall cathodic reaction.

Figure 3c presents the influence of ammonia on copper corrosion. It can be seen that ammonia enhanced the anodic reaction, resulting in a shift of the polarization curve to the right. Correspondingly the corrosion potential decreased, and the corrosion current density increased (Table 1). The anodic reaction of copper corrosion is the oxidation of elemental copper to cuprous ion Cu^+, which, in the absence of ammonia, has very low solubility and can form $Cu_2O(s)$ on the copper surface.[1] The $Cu_2O(s)$ layer retards the further oxidation of copper base metal. This reaction provides corrosion resistance for copper and makes it a feasible heat exchanger component. However, in the presence of ammonia, the solubility of cuprous ion is increased through complexation with ammonia,[14] weakening the
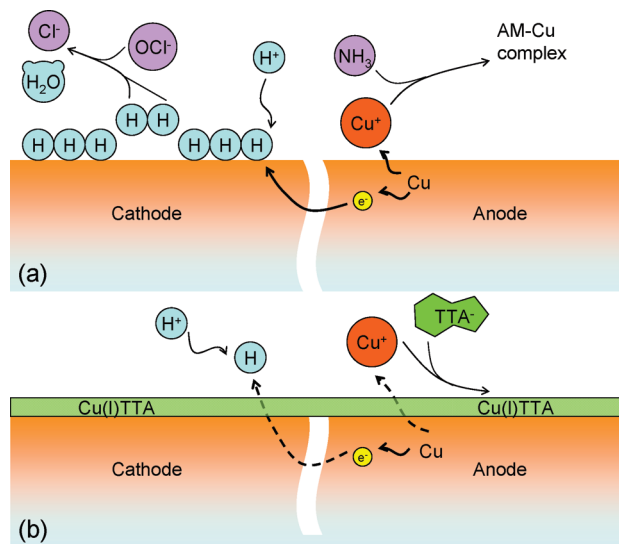
Figure 4. Schematics of mechanisms of the influence of TTA and free chlorine, monochloramine, and ammonia on copper corrosion. (a) Free chlorine and monochloramine act as depolarizers which remove hydrogen atoms from the cathodic surface, causing a higher copper corrosion rate; ammonia complexes cupric ion and increases the solubility of copper. (b) TTA forms a protective layer on the cathodic and anodic surfaces.

protective $Cu_2O(s)$ film on the copper surface. In this study, ammonia enhanced the anodic reaction of copper corrosion, suggesting the weakening of the protective $Cu_2O(s)$ film.

Figure 3d shows the influence of TTA alone on copper corrosion. TTA retarded both anodic and cathodic reactions, and especially the anodic reaction. The polarization resistance curve shifted to the left, and the corrosion current density decreased (Table 1). Although the corrosion potential shifted toward more negative, the shift was not as significant as compared to the shifts caused by free chlorine and monochloramine. This is because TTA inhibited both anodic and cathodic reactions but not preferentially for a particular reaction. The retardation effect was strengthened with increasing TTA dose. Several studies have shown that TTA forms a polymeric film of Cu(I)-TTA on the copper surface.[6−8] Results obtained in this study showed that the polymeric film can form both on cathodic and anodic areas, thus significantly retarding the corrosion reaction.

The schematic diagram in Figure 4 summarizes the mechanisms of the influence of TTA, free chlorine, monochloramine, and ammonia on the anodic and cathodic reactions involved in copper corrosion. In the cathodic reaction depicted in Figure 4a, the action of free chlorine as a depolarizer is shown, including the removal of hydrogen atoms adsorbed on the cathodic surface, which accelerates the overall corrosion reaction rate. Monochloramine enhances the cathodic reaction by a similar mechanism. The anodic area in Figure 4a shows that cuprous ions form complexes with ammonia, enhancing the dissolution of copper into solution. Figure 4b shows that, in the presence of TTA, a polymeric film of Cu(I)-TTA forms on the surface of copper and inhibits both cathodic and anodic reactions.

3.2. Interinfluences between TTA and Free Chlorine, Monochloramine, and Ammonia on Copper Anodic and Cathodic Corrosion Reactions. Figure 5a presents the interinfluence between TTA and free chlorine on copper anodic and cathodic behaviors. In the presence of TTA, the additional presence of free chlorine enhanced the anodic reaction and increased the corrosion potential and the corrosion current density (Table 1). In the presence of free chlorine, the addition
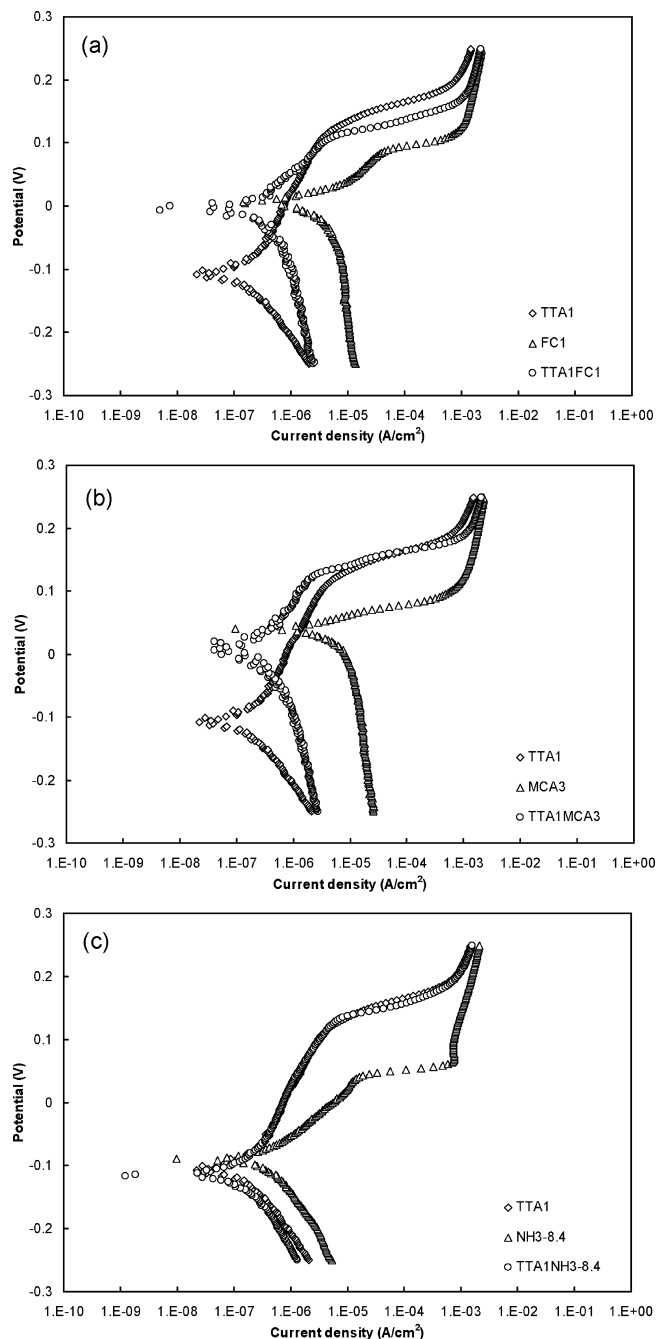

Figure 5. Interinfluence on copper corrosion of TTA 1 ppm and (a) free chlorine (FC) 1 ppm as Cl_2, (b) monochloramine (MCA) 3 ppm as Cl_2, and (c) ammonia (NH_3) 8.4 ppm as N (where, for example, 1E-10 represents 1×10^{-10}). It can be seen that TTA retarded corrosion of copper significantly in the presence of FC and MCA and thoroughly in the presence of ammonia.

of TTA retarded both the anodic and cathodic reactions. The corrosion current was lowered with a slight decrease of corrosion potential (Table 1).

Figure 5b presents the interinfluence between TTA and monochloramine on the copper anodic and cathodic behaviors. The similarity between Figure 5a and Figure 5b indicates that TTA also retarded both the anodic and cathodic reactions of copper corrosion in the presence of monochloramine.

Figure 5c shows the interinfluence between TTA and ammonia on copper anodic and cathodic behaviors. It was found that, in the presence of TTA, the addition of ammonia influenced neither the anodic nor the cathodic reaction. In the presence of ammonia, the additional presence of TTA retarded both the
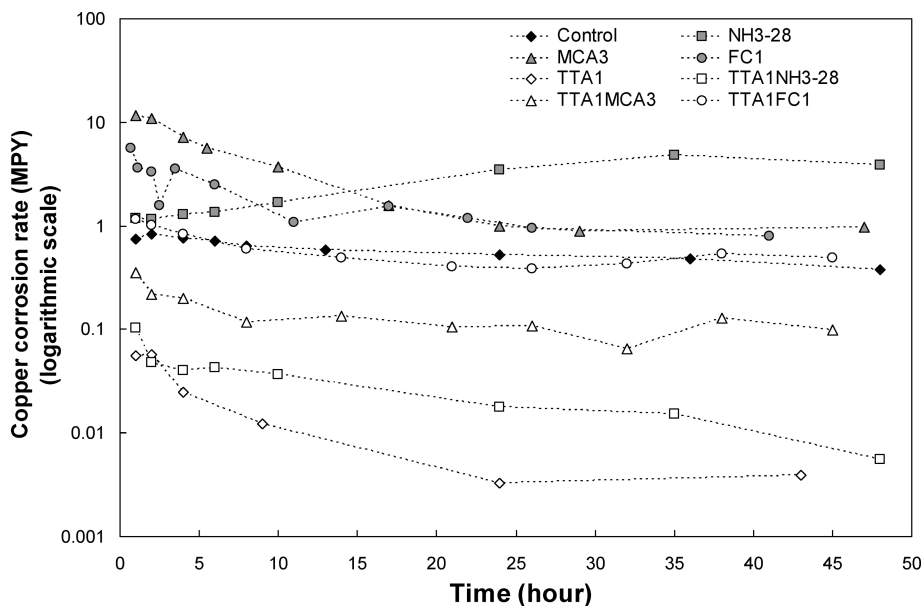
Figure 6. Copper corrosion rate monitoring with time under the influence of TTA (1 ppm) and free chlorine (FC, 1 ppm as Cl_2), monochloramine (MCA, 3 ppm as Cl_2), and ammonia (NH_3, 28 ppm as N). TTA effectively protected the copper surface against monochloramine and ammonia. TTA's protection against free chlorine was not satisfactory.

anodic and cathodic reactions. The corrosion current was lowered with a slight decrease of open-circuit potential (Table 1). Thus, in the presence of TTA, the influence of ammonia on copper corrosion was negligible.

3.3. Copper Corrosion Rate in the Presence/Absence of TTA, Ammonia, Monochloramine, and/or Free Chlorine in Synthetic Cooling Water. Figure 6 presents the results of a 2 day, semicontinuous instantaneous corrosion rate monitoring of copper in synthetic cooling water with the addition of TTA, free chlorine, monochloramine, and/or ammonia. The corrosion rate was determined from polarization resistance measurements.[31] The y-axis in Figure 6 is shown in logarithmic scale since the measured corrosion rate spanned 4 orders of magnitude. As expected, when TTA was absent, the corrosion rate of copper increased in the presence of free chlorine, monochloramine, and ammonia relative to the control system. Ammonia increased the corrosion rate of copper 10-fold.

On the other hand, TTA significantly decreased the corrosion rate by 2 orders of magnitude compared to the control. Even in the presence of ammonia, the corrosion rate was still low, 3 orders of magnitude lower than the case in which ammonia was present but TTA absent. The presence of TTA also mitigated the aggressiveness of monochloramine and decreased the corrosion rate 10-fold. However, the presence of TTA only lowered the corrosion rate of copper slightly in the presence of free chlorine. If the generally acceptable corrosion rate for copper alloy used in cooling water system heat exchangers of 0.3 mils/year is considered,[32] the presence of TTA is necessary in a cooling water system with ammonia or monochloramine. Even with TTA present, free chlorine made the corrosion rate unacceptable.

The implication of these results is that, in cooling systems using secondary treated municipal wastewater as makeup water, TTA is a good copper corrosion inhibitor and can protect copper well against ammonia and monochloramine. TTA's protection of copper against free chlorine is not as effective as that with monochloramine. Thus, monochloramine appears to be a better biomass growth control agent than free chlorine in terms of copper corrosion protection, in addition to its greater or similar ability to control biofouling than free chlorine.[24,25]

Figure 6 also indicates that the copper corrosion inhibition by TTA was further enhanced with time (open diamonds) because the TTA adsorption onto copper took time to reach equilibrium. By comparing the open and solid diamonds in Figure 6, the 1 ppm TTA corrosion inhibition efficiency reached approximately 99% after 1 day exposure, which was even higher than the 75% inhibition efficiency of 20 ppm TTA after 1 h exposure, shown in Table 1. The inhibition efficiency remained at approximately 99% for another day. A pilot-scale study on TTA corrosion inhibition for copper in contact with concentrated (4×), corrosive abandoned mine drainage showed that 2 ppm TTA had inhibition efficiency of 86−90% over an experimental period of 21 days.[26]

3.4. Stability of TTA in the Presence/Absence of Free Chlorine, Monochloramine, Ammonia, and/or Copper Specimens. Figure 7 shows the stability of TTA in the presence/absence of free chlorine, monochloramine, ammonia, and/or copper specimens. It was found that, over a 10 h testing period, TTA was very stable in synthetic cooling water when ammonia or monochloramine was added in the absence of copper specimens. In the presence of free chlorine and in the absence of copper specimens, a small fraction of TTA (around 10%) was depleted during the first hour after free chlorine addition and then remained stable for the next 8 h. The depletion was due to the formation of chlorotolyltriazole, which can rapidly revert to TTA in the absence of free chlorine.[4]

In the presence of copper specimens, TTA was depleted 10% in the first hour due to TTA adsorption onto the copper surface and then remained relatively stable without any other chemical addition or with the addition of ammonia. In the case where free chlorine was added, TTA depleted rapidly. The addition of monochloramine also caused some TTA depletion. The depletion of TTA in the presence of free chlorine/monochloramine and copper specimens was due to the catalytic effect of Cu for free chlorine/monochloramine to degrade TTA, as discussed below.

3.5. TTA Adsorption Film Analysis. Figure 8 shows the results of mass analysis of TTA in synthetic cooling water in the presence of copper specimens, ammonia, monochloramine,
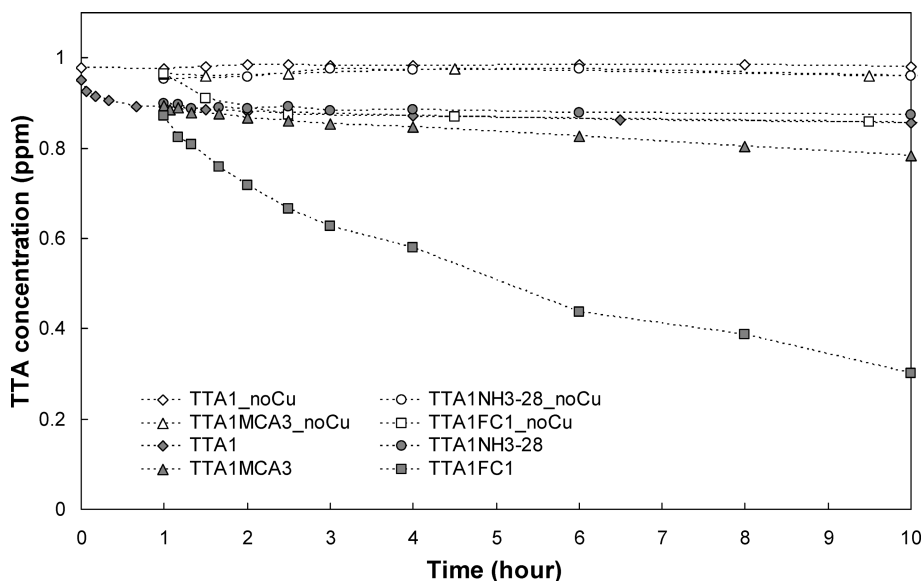
Figure 7. Depletion of TTA (initially 1 ppm) in synthetic cooling water under different conditions.
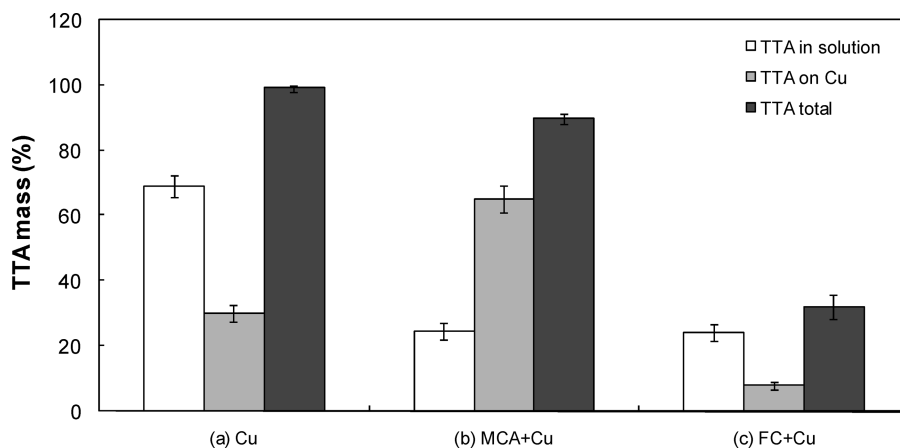

Figure 8. Mass balance analysis of TTA in solution (a) in the presence of copper, (b) in the presence of copper and monochloramine, and (c) in the presence of copper and free chlorine. The error bars for a represent the standard deviation of a triplicate analysis and for b and c represent the difference of a duplicate analysis. The results indicate that, in the absence of monochloramine and free chlorine, TTA mass was well-balanced. In the presence of monochloramine, approximately 10% of TTA was degraded and more TTA was absorbed on the copper surface. In the presence free chlorine, more than 60% of TTA was degraded and only a small amount of TTA was absorbed on the copper surface.

and/or free chlorine in 2 h tests conducted in a 0.125 mL reactor. Triplicate tests (a) in Figure 8 showed that, in the presence of copper specimens, TTA in solution was consumed but TTA mass in the system was constant; i.e., the depletion of TTA mass in the solution was equal to the mass of TTA adsorbed on copper. The triplicate analysis was performed initially to confirm the reproducibility of the TTA film analysis technique, and the satisfactory mass balance of TTA in tests a indicated that the technique used to analyze the TTA film was reliable. Thus, duplicate analyses were performed in other tests, and those tests also showed satisfactory reproducibility. Duplicate tests b showed that in the presence of monochloramine, TTA in solution was depleted more severely than in tests a. Most TTA mass depleted was recovered from the copper surface. The total mass loss of TTA in the system was about 10%. Thus, monochloramine caused more TTA adsorption on the copper surface, indicating the TTA film might have higher packing density, more adsorbed layers, or both, assuming the film is homogeneous over the copper surface. Duplicate tests c showed that, in the presence of free chlorine, TTA in solution was depleted to a degree similar to b. However, TTA mass on the copper surface in c was significantly lower than in test b. The mass of

TTA in the system was far from being recovered, and nearly 70% of TTA mass was lost. Thus, the results suggested that the copper surface worked as a catalyst for free chlorine to degrade TTA. The catalytic effect of copper for monochloramine to degrade TTA was not as noticeable as that for free chlorine.

Figure 9 shows the TTA depletion kinetic in the presence of copper. Since monochloramine and free chlorine were not present, the amount of depletion of TTA in the solution should be equal to the amount of adsorption of TTA onto copper, as supported by b in Figure 8. As shown in Figure 9, the depletion rates of TTA decreased dramatically in the initial hours and then reached relatively low and stable values among all tests with various initial TTA concentrations ranging from 0.027 to 0.2 ppm. Figure 9 also indicates that the higher the initial TTA concentration, the higher the initial adsorption rate. Thus, a higher initial TTA concentration should result in higher initial inhibition efficiency, which is supported by the inhibition efficiency determined after 1 h copper exposure (Table 1). Mass of TTA adsorbed on copper for all tests was also measured for the purpose of total TTA mass balance, and satisfactory total mass recovery percentages were obtained (96 to 100%, except
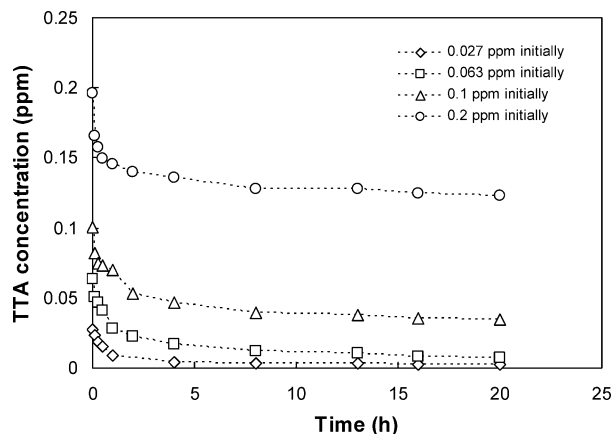
Figure 9. TTA depletion kinetics in synthetic cooling for selected tests with initial TTA concentrations ranging from 0.027 to 0.2 ppm. The higher the initial TTA concentration, the faster the depletion kinetics, that is, the higher the adsorption kinetics.
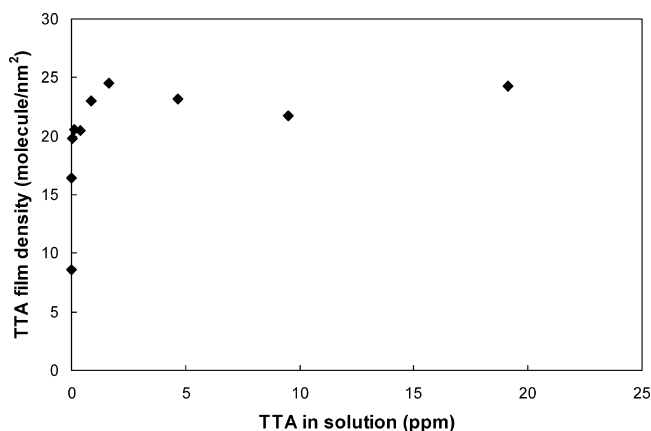

Figure 10. Isotherm for TTA adsorption on copper. Data acquired after 20 h of Cu specimen immersion (equilibrium reached after 20 h immersion).

for the test with the lowest TTA initial concentration, 0.027 ppm, which had a recovery percentage of 112%).

Additional tests with initial TTA concentrations ranging from 0.5 to 20 ppm were also performed, and TTA concentration in solution and TTA mass on copper were measured after 20 h of immersion. Continuous monitoring of TTA in solution was not performed since the amount of TTA mass depletion was relatively negligible compared to the total TTA mass in the solution. Figure 10 shows the TTA adsorption isotherm onto copper.

The calculated adsorption film density reached approximately 20−25 molecules/nm². Considering that the projection area of a Cu(I)-TTA complex is about 0.25−0.37 nm² (calculated using MarvinSketch 5.2.0, ChemAxon, Ltd.), the TTA polymeric film on copper can be estimated as being about 5.0−9.3 layers. Because the projection radius of the Cu(I)-TTA molecule is 0.35−0.52 nm, the film thickness can be estimated to be 3.6−9.4 nm, which is similar to previous estimates: 3 nm for 4-methyl-benzotriazole and 7 nm for 5-methylbenzotriazole.[6] However, Figure 8 suggests that, in the presence of monochloramine, the TTA film could have a higher packing density, a greater number of layers, or both, assuming the film is homogeneous over the copper surface. The reason for the higher packing density might be that the higher corrosion rate in the presence of monochloramine provided more oxidized copper atoms which bridged between TTA molecules on the surface.
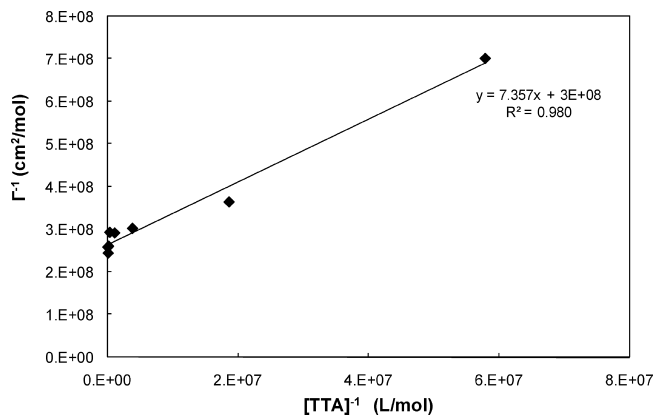

Figure 11. Plot of Γ^{-1} vs $[TTA]^{-1}$ (where, for example, 8.E+08 represents 8.0×10^8). The linear relationship indicates the adsorption is a Langmuir type. It was estimated from this figure that the maximum adsorption concentration, Γ_{max}, was 3.8×10^{-9} mol/cm² and the adsorption equilibrium constant, K_{ads}, was 3.6×10^7 L/mol.

3.6. TTA Free Energy of Adsorption on Copper. The adsorbed TTA concentrations determined from surface film analysis were used to prepare adsorption isotherms. It was determined that a Langmuir isotherm could fit the adsorption data reasonably well, suggesting site-limited chemisorptions and enabling an estimation of the free energy of TTA adsorption on copper.

It is generally recognized that the free energy of adsorption (ΔG°_{ads}) can be an indicator of whether the adsorption is physisorption (if ΔG°_{ads} less negative than −20 kJ/mol) or chemisorption (if ΔG°_{ads} is around −40 kJ/mol or more negative).[33] Since it has been proposed that the TTA adsorption on copper is through chemisorption,[6,9] the free energy of adsorption should be around −40 kJ/mol or more negative.

The stoichiometry of TTA adsorption on Cu can be written as

$$TTA + \equiv Cu \leftrightarrow \equiv CuTTA \tag{1}$$

From the principle of mass action, the adsorption equilibrium constant K_{ads} (L/mol) in the dilute aqueous solution can be expressed as

$$K_{ads} = \frac{[\equiv CuTTA]}{[TTA][\equiv Cu]} \tag{2}$$

where $[TTA]$ is the free TTA concentration in solution (mol/L), $[\equiv CuTTA]$ is the concentration of copper−TTA surface complexes (mol/cm²), and $[\equiv Cu]$ is the surface concentration of free (unoccupied) adsorption sites (mol/cm²). If Γ is used to represent $[\equiv CuTTA]$, the maximum adsorbed concentration, Γ_{max} is equal to the summation of $[\equiv CuTTA]$ and $[\equiv Cu]$. Equation 2 can be rewritten in linearized form as

$$\Gamma^{-1} = \Gamma_{max}^{-1} + \Gamma_{max}^{-1} K_{ads}^{-1}[TTA]^{-1} \tag{3}$$

By plotting Γ^{-1} vs $[TTA]^{-1}$, the intercept and the slope are Γ_{max}^{-1} and $K_{ads}^{-1}\Gamma_{max}^{-1}$, respectively. Data points of TTA concentration in the range of 0−5 ppm in Figure 10 were used to derive the Γ^{-1} vs $[TTA]^{-1}$ plot as shown in Figure 11. It was estimated from Figure 11 that Γ_{max} was 3.8×10^{-9} mol/cm² and K_{ads} was 3.6×10^7 L/mol. The free energy of adsorption can be calculated through the following equation:[14]

$$\Delta G^\circ_{ads} = -RT \ln K_{ads} \tag{4}$$

where R is the gas constant (8.314 J/(mol·K)) and T is the absolute temperature (298 K). $\Delta G°_{ads}$ is calculated to be −43.1 kJ/mol, which is in the range of values typical of chemisorption reactions.

The Langmurian TTA adsorption on copper and the surface film analysis indication that multilayer adsorption occurs seems contradictory, since Langmuir adsorption usually implies monolayer adsorption. A possible explanation is that oxidized and released copper ions could serve as additional adsorption sites for TTA to form the polymeric Cu(I)TTA adsorption layers, a mechanism similar to BTA adsorption on copper proposed by Ling and Han.[7] The shape of an isotherm plot is not definitive evidence of a particular adsorption mechanism. Equivalently, a different adsorption mechanism can yield similar isotherm plots.

4. Summary and Conclusions

In this study, the effectiveness of TTA, a commonly used inhibitor of copper corrosion in cooling systems, was studied in the presence of free chlorine, monochloramine, and ammonia. These corrosive constituents were selected as they are present in secondary treated wastewater which is of interest for use in cooling systems in some regions. The influence of various combinations of these agents on copper anodic and cathodic reactions was studied via electrochemical potentiodynamic polarization and polarization resistance measurements. TTA's stability in synthetic cooling water and in the presence of free chlorine, monochloramine, and ammonia was also examined. The thickness of the TTA adsorption film on copper in the presence of free chlorine, monochloramine, and ammonia was quantitatively established.

The electrochemical polarization resistance measurements in synthetic cooling water showed that free chlorine, monochloramine, and ammonia enhanced the corrosion rate of copper in the absence of TTA. When TTA was present, the aggressiveness of free chlorine to copper was reduced but still caused unacceptable copper corrosion rates. TTA effectively mitigated the aggressiveness of monochloramine and yielded a copper corrosion rate 1 order of magnitude lower than in the case in which TTA was absent. TTA protected copper from corrosion by ammonia very effectively. Thus, in the application of secondary treated municipal wastewater as power plant cooling system makeup water, monochloramine was found to be a much better biomass control agent than free chlorine in terms of copper corrosion.

The electrochemical potentiodynamic polarization measurements in synthetic cooling water were conducted to investigate the TTA copper protection mechanism in the presence of free chlorine, monochloramine, and ammonia. It was found that free chlorine and monochloramine likely act as depolarizers that remove hydrogen atoms from the copper surface and accelerate copper corrosion. Ammonia and Cu(I) form surface complexes and thus enhance Cu(I) dissolution. TTA formed a protective film on the copper surface, and both the anodic and cathodic reactions were retarded against the aggressiveness of free chlorine, monochloramine, and ammonia.

The TTA adsorption film analysis showed that the copper surface worked as a catalyst for free chlorine to degrade TTA. The catalysis effect was not significant for monochloramine. In the absence of free chlorine, monochloramine, and ammonia, the adsorption of TTA was fast, and the packing density reached a relatively stable value of 20−25 molecules/nm² after hours of contact with copper. The film seemed to grow further but at very low rate. The film was estimated to be 5−9.3 layers with the thickness of 3.6−9.4 nm. While the TTA adsorption appeared to form several layers on the copper surface, the adsorption data were well-described by a Langmuir type isotherm, and the calculated free energy of adsorption of 43 kJ/mol indicated chemisorption.

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