Biocorrosion of mild steel and copper used in cooling tower water and its control

Xiao Lei Li¹ · Jayaraman Narenkumar² · Aruliah Rajasekar² · Yen-Peng Ting¹

Received: 30 September 2017 / Accepted: 3 March 2018 / Published online: 12 March 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

The present study describes the biocorrosion of mild steel (MS1010) and pure copper (Cu) in cooling water environments (both field and lab study). Electrochemical and surface analyses of both metals were carried out to confirm the corrosion susceptibility in the presence of bacteria and inhibitor. Surface analysis of the MS and Cu coupons revealed that biofilm was developed with increasing exposure time in the field study. In the lab study, accumulation of extracellular polymeric substance over the metal surface was noticed and led to the severe pitting type of corrosion on both metal surfaces. Besides, the anti-corrosive study was carried out using the combinations of commercial corrosion inhibitor (S7653—10 ppm) with biocide (F5100—5 ppm), and the results reveal that the corrosion rate of MS and Cu was highly reduced to 0.0281 and 0.0021 mm/year (inhibitor system) than 0.1589 and 0.0177 mm/year (control system). Inhibition efficiency for both metals in the presence of inhibitor with biocide was found as 82 and 88% for MS and Cu, respectively. The present study concluded that MS was very susceptible to biocorrosion, compared to copper metal in cooling water environment. Further, the combination of the both inhibitor and biocide was effectively inhibiting the biocorrosion which was due to its antibacterial and anti-corrosive properties.

Keywords Biocorrosion · Cooling tower · Copper · Mild steel · EIS · SEM–EDX

Introduction

Corrosion is a pervasive problem encountered in designing cooling water treatment programs (Flemming 1996; Rajasekar and Ting 2011; Narenkumar et al. 2017a, 2018). In natural and artificial environments, corrosion occurs when materials made of pure metals/alloys undergo a substance change from the ground state to an ionized species (Booth

1971). Corrosion is an electrochemical reaction and containing of an anodic reaction involving the oxidation of the metal surface (corrosion reaction), and a cathodic reaction involving the reduction of ions (Beech and Gaylarde 1999; Wang et al. 2006; Rajasekar et al. 2007; Parthipan et al. 2017a). These reactions can be accelerated by microbial communities while organisms are in close contact with the metal surface and forms a biofilm which causes the metal deterioration (Fontana 1986; Wang 2015; Narenkumar et al. 2016; Parthipan et al. 2017b). Biofilms consist of microbial community of cells and the extracellular polymeric substances (EPS), which facilitate the attachment of cells on the metal surface and inorganic precipitates derived from the corrosion products of the metal substratum (Jayaraman et al. 1997; Harrah et al. 2004; Rajasekar and Ting 2011). Cooling towers are used in industries for heat transfer without the need for refrigerant. Cooling towers function by transferring heat from recirculating water into atmosphere (MacDonald and Brözel 2000). These towers provide a unique atmosphere and typically maintain the temperature between 25 and 35 °C which favour the microbial growth and dissemination (Wagner and Little 1993; Xu et al. 2012; Colombol and

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13205-018-1196-0>) contains supplementary material, which is available to authorized users.

✉ Aruliah Rajasekar
rajasekargood@gmail.com; rajsekar.aruliah@gmail.com

✉ Yen-Peng Ting
chetyp@nus.edu.sg

¹ Department of Chemical and Biomolecular Engineering, National University of Singapore, Kent Ridge 117576, Singapore

² Environmental Molecular Microbiology Research Laboratory, Department of Biotechnology, Thiruvalluvar University, Serkkadu, Vellore 632 115, India

Trasatt 2018). Both substrata and microbes present in the incoming water lead to the presence of microorganism in the cooling water system.

Copper and copper alloy metals are widely used in industrial applications due to high conductivity, excellent corrosion resistance and mechanical workability. Cu is mostly used in electrical lines, heating, cooling systems, pipelines and sea water transport (Martinez et al. 2004). MS material is also widely used in pipelines to transport water to cooling tower (El-Shamy et al. 2009). The rust has a negative effect on heat transfer and thus decreases in cooling efficiency of the equipment (Narenkumar et al. 2017b). In this present investigation, the impact of biofilm on biocorrosion of MS and Cu in the cooling water system is evaluated using EIS and WL methods. The effect of dosage concentration of the biocide and corrosion inhibitor is also investigated.

Materials and method

Background information of the cooling tower water

The cooling tower, located in Teijin Polycarbonate Singapore Pte Ltd, Singapore (1.2635°N, 103.6946°E), has a dimension of 9.4 m × 6.8 m × 1.5 m (water depth) and a capacity of 2000 m³/h. The cooling water was supplied by SembCorp Utilities and Terminal (SUT) and maintained at about 31.2 ± 2 °C. The physiochemical parameters of the cooling tower water was estimated by Himedia kit.

Enumeration of bacteria

A sample of water was collected at a cooling tower using sterilized conical flasks and transported in an ice box to the laboratory. The samples were serially diluted (tenfold) and subjected to pour plate technique for aerobic bacterial isolation. Nutrient agar was used to enumerate heterotrophic bacteria (HB). After the incubation of the plates at 30 °C for 24 h, the total viable count was enumerated (Rajasekar and Ting 2014). The isolated bacterial strains were used as mixed cultures for the biocorrosion study (Lab study).

Metal sample preparation

MS1010 coupons containing 0.37% silicon, 1.24% manganese, 0.026% sulphur 0.027% phosphorus, 0.19% copper, 0.16% carbon 0.007% nitrogen, 0.02% aluminium, and 97.96% iron and Cu coupons (purity > 99.9%) were exposed to the cooling tower water to examine susceptibility of the metal to biofilm formation.

Before the experiment, all the coupons were sequentially ground with a silicon carbide paper (180, 500, 800, 1200 and 1500 grades) to a smooth surface, and ultimately polished to

a mirror finish surface by 0.3 µm alumina powder. The mirror finish coupons were rinsed with sterile dis H₂O, and 70% ethanol for surface sterilized and finally stored in a desiccator. Coupons of three different sizes were used in the present study: (a) round coupon with diameter of 10 mm for EIS and Fourier transform infrared spectroscopy (FTIR analysis); (b) round coupon with diameter of 8 mm for scanning electron microscope (SEM) observation; and (c) 7.5 cm × 1 cm and a 0.1-cm thick coupon for WL experiment.

Corrosion studies

Field study

Polished MS 1010 and Cu metal coupons were exposed to the cooling tower water system in the field condition. After different time intervals (10, 25, 35 and 90 days), both types of coupons were removed and subjected to the WL, EIS and surface analyses. For WL determination, the metal coupons were pickled in Clark solution (hydrochloric acid—1 L, antimony trioxide—20 g, stannous chloride—50 g) and washed in dis H₂O and dried with an air drier. Triplicate experiments were run for each system. The final weights of the coupons in every systems and time intervals were taken, and the corrosion rate was calculated following the NACE standard protocol (NACE 2005).

Laboratory study

The electrolyte used in the laboratory study was cooling water collected from the cooling tower at Teijin Polycarbonate Singapore Pte Ltd. A commercial corrosion inhibitor (KURITA, S-7653) composed of polyphosphate, phosphate, zinc salts and a polymer was used as a scale inhibitor, and a bacteria control agent (KURITA, F-5100) was used as a biocide to control slime-producing bacteria. Biocorrosion experiments were initiated by hanging sterile mirror finish MS and Cu coupons on a nylon thread in both with and without the bacteria/corrosion inhibitor (S7653)/biocide (F-5100) (Rajasekar and Ting 2014; Narenkumar et al. 2017b). The experimental scheme is shown in Table 1. At the end of the experimental system (10 days), the coupons were removed and subjected to EIS (polarization), FTIR and SEM–EDX analysis. For systems 3–6, 1% nutrient broth was added as an energy source for bacterial growth. Bacterial culture was enumerated for both Cu and MS coupons in the simulated cooling water system.

Electrochemical study

Corrosion characterization of MS and Cu (field study) metals was carried using EIS. Potentiodynamic polarization

Table 1 The experimental scheme of biocorrosion system (lab study)

S. no.	Systems	Experimental scheme
1	System 1	400 mL of sterile cooling tower water
2	System 2	400 mL of sterile cooling tower water with the inhibitor at 10 ppm
3	System 3	400 mL of sterile cooling tower water with 1 mL of overnight mixed consortium (1.4×10^4 CFU/mL)
4	System 4	400 mL of sterile cooling tower water consisted of 1 mL of overnight mixed consortium with inhibitor (10 ppm)
5	System 5	400 mL of sterile cooling tower water consisted of 1 mL of overnight mixed consortium with biocide (5 ppm)
6	System 6	400 mL of sterile cooling tower water consisted of 1 mL of overnight mixed consortium with the corrosion inhibitor (10 ppm) and biocide (5 ppm)

(GPES) was conducted using Autolab PGSTAT101 (Eco Chemie, B.V., Holland). Each experiment was subjected in a three-electrode electrochemical cell, with an Ag/AgCl electrode (Metrohm Pte, Ltd) as the reference electrode and a platinum electrode as the counter electrode. EIS measurements were performed *ex situ*; the coupons removed in each system were embedded from sample holder in the corrosion cell (purchased from Metrohm Pte, Ltd). The exposed surface area of 0.785 cm^2 performs as the working electrode. ES measurement procedures were adopted from our earlier studies (Rajasekar et al. 2008, 2017; Narenkumar et al. 2017c).

Surface analysis

At the end of the corrosion experiment, the coupons were subjected to SEM to assess the bacterial assemblage. The biofilm on the metal surface was fixed using 3% glutaraldehyde in a phosphate-buffered solution overnight and washed with ethanol serially (25, 50, 75–95% concentration) (Rajasekar et al. 2007). The samples were subsequently dried and stored in desiccators before they were visualized after platinum coating with SEM (Jeol JSM5600) operating in beam voltage of 15 kV. To analyse biofilm formation on metal coupon (MS and Cu), the surfaces were examined

using an FTIR (Bio-Rad Model: FTS 135) (Rajasekar and Ting 2014).

Results and discussion

Field study

Bacterial enumeration

The physiochemical properties of cooling tower water pH, alkalinity, hardness and chloride were observed as 8.5, 157, 122 and 235 mg/L, respectively. The total viable heterotrophic bacteria in the cooling waste sample was found to be 2.12×10^4 CFU/mL and confirmed the occurrence of bacteria in the cooling water.

Weight loss study

Weight loss data for Cu and MS metal coupons at different exposure time intervals in the cooling tower water are presented in Table 2. Cu and MS weight loss on exposure for 10 days was found to be 0.0198 and 0.231 g, and increased with exposure time. The data reveal that more severe corrosion occurred for MS (0.802 g) than Cu (0.048 g) in the cooling water environment. Examination

Table 2 Weight loss data for the copper and mild steel at different time exposures at cooling tower water (field study)

Exposure time (days)	Copper (g)				Mild steel (g)			
	Initial weight (W_0)	Final weight (W_f)	Weight loss (W_l)	Corrosion rate (mm/year)	Initial weight (W_0)	Final weight (W_f)	Weight loss (W_l)	Corrosion rate (mm/year)
10	5.016	4.9963	0.0197	0.0477	5.83	5.5987	0.2313	0.6379
25	4.905	4.8792	0.0236	0.0249	6.12	5.7432	0.3768	0.4157
35	4.95	4.9236	0.0264	0.0183	5.91	5.5122	0.3978	0.3135
45	4.995	4.968	0.027	0.0145	5.74	5.2812	0.4588	0.2812
50	4.896	4.8656	0.0304	0.0147	5.42	4.9327	0.4873	0.2688
60	4.861	4.8298	0.0312	0.0126	5.75	5.2296	0.5204	0.2392
90	4.945	4.8993	0.0457	0.0123	5.56	4.82315	0.73685	0.2258

of the data showed that weight loss increases with corrosion rates decreasing over time. This observation was adopted by Ma et al. (2010) that corrosion rates initially increased then decreases and again suddenly increased in the marine environment. It can be concluded that the corrosion of MS was more severe corrosion than Cu in the cooling water environment with exposure time (Narenkumar et al. 2016).

Electrochemical study

From the polarization study (Table 3 and Fig S1), the corrosion current density of the Cu metal at different time periods (10, 25, 35, 45, 50, 60, 90 days) was found to be 2.29×10^{-7} , 1.24×10^{-10} , 8.09×10^{-10} , 4.23×10^{-7} , 2.4×10^{-7} , 1.16×10^{-7} , 2.27×10^{-6} A/cm², respectively. It can be concluded that initially (10th day) the dissolution of Cu (2.29×10^{-7} A/cm²) was high when compared to MS (2.96×10^{-8} A/cm²). Over time, a thick corrosion product formed on the Cu metal surface and decreases current density. On the 90th day, however, the I_{corr} value was found to be higher in Cu (2.27×10^{-6} A/cm²) due to the removal of the thick corrosion product. MS showed a higher I_{corr} value (3.38×10^{-7}) compared to Cu (8.09×10^{-10}) for the 35th day sample. Polarization data revealed that MS was more prone to corrosion at the exposure time of 35th day. But the Cu metal only after the exposure time of 60 days. It can be concluded that, compared to MS, the higher corrosion resistance of Cu protective film was due to the Cu²⁺ ions toxicity to the bacterial growth (Fonseca et al. 2004). The WL data were also consistent with the polarization data.

Surface analysis

SEM analysis

The SEM of Cu at different exposure times (Fig. 1) showed the development of biofilm and its increase in the exposure time. SEM of MS after 10th day (Fig. 1b1) showed the thicker biofilm formation on the surface compared to the Cu. MIC was linked to cellular adhesion and extracellular polymeric substances (EPS) produced during biofilm formation. These adhesion processes and the subsequent EPS production lead to an important modification of the metal interface. Its partial or total coverage by strongly adherent biofilms produces a barrier to the exchange of elements between the metal surface and the aqueous environment. Important changes in the type and concentration of ions, pH and redox condition were induced by the biofilm, altering the passive behaviour of the metal substratum and its corrosion products, as well as the electrochemical parameters used to assess corrosion rates. Hence, in the present study, the higher production of EPS influences the differential aeration on metal surfaces which results altering the pH and redox reactions (potential difference) on the metal surfaces which leads to acceleration of corrosion product (Shameer 2016; Booth 1971; Narenkumar et al. 2018).

FTIR analysis

FTIR pattern of the biofilm formed on Cu and MS coupons exposed to cooling water at different time intervals is shown in Fig. 2. The distinct peaks at 1000 cm⁻¹ were observed in the IR spectrum are assigned to the C–O group of polysaccharides. A broad band was noticed in the range

Table 3 Polarization data for copper and mild steel at different time exposures in cooling tower water (field study)

Exposure time (days)	Metal	Corrosion potential E_{corr} (mV)	Current density I_{corr} (A/cm ²)	B_a (V/dec)	B_c (V/dec)	Polarization resistance (R_p) (Ohm)	Corrosion rate CR (mm/year)
10	Cu	− 138	2.29E−07	0.064	0.147	2.28E+04	2.35E−03
	MS	− 120	2.96E−08	0.029	0.002	9.09E+03	3.49E−04
25	Cu	− 200	1.24E−06	0.129	0.312	1.78E+04	1.28E−02
	MS	− 366	1.94E−10	0.250	0.114	8.15E+07	2.28E−06
35	Cu	− 0.06	8.09E−10	0.189	0.106	1.36E+07	8.32E−06
	MS	− 133	3.38E−07	0.089	0.130	1.90E+04	3.96E−03
45	Cu	− 104	4.23E−07	0.096	0.140	1.76E+04	4.34E−03
	MS	− 233	9.92E−07	0.113	0.292	1.84E+04	1.17E−02
50	Cu	− 0.96	2.4E−07	0.077	0.116	2.05E+04	2.47E−03
	MS	− 368	2.96E−06	0.119	0.437	9.72E+03	3.47E−02
60	Cu	− 101	1.16E−07	0.146	0.178	1.23E+05	1.19E−03
	MS	− 130	1.12E−06	0.820	0.166	6.66E+03	1.32E−02
90	Cu	− 130	2.27E−06	0.254	0.653	4.40E+04	2.33E−02
	MS	− 202	1.18E−06	0.121	0.269	1.52E+04	1.38E−02

Fig. 1 SEM image of copper (a, b, c, d, e) and mild steel (a1, b1, c1, d1, e1) coupons immersed in cooling tower water (field study) (5000× magnification). a, a1 fresh copper, b, b1 10 days, c, c1 60 days, d, d1 75 days, e, e1 90 days

Fig. 2 FTIR spectrum of copper and mild steel samples at duration of exposure in cooling tower water (field study) **a** copper, **b** mild steel

of 3000–3500 cm^{-1} which may indicate the presence of adsorbed water molecule and OH or NH groups (Baars 1930; De la Fuente et al. 2011). The band at 1650 cm^{-1} corresponds to amide-I (Obuekwe et al. 1981) and the intensity lesser peak 1500 cm^{-1} assigned to the symmetric deformation of the NH_3^+ group of zwitterions adhesion on the surface of Cu and MS. A strong band was noticed at the range of 1675–1620 cm^{-1} which assigned to the C=O stretching vibration. The peak at 1242–1254 cm^{-1} stretching

vibration may indicate the presence of –OH group. The bands at 450–700 cm^{-1} may have originated from $\gamma\text{-Fe}_2\text{O}_3$ (670 cm^{-1}). The biofilms exhibit peaks of high intensity in MS when compared to Cu, and showed the susceptibility of MS 1010 to form biofilm. FTIR results indicated that Cu and MS are very susceptible to biofilm formation.

Lab study

Weight loss study

The WL data for MS and Cu metal coupons at different systems in simulated cooling tower water are presented in Table 4. In System 1, the WL of MS and Cu was about 0.0576 and 0.0479 g, respectively. In the presence of corrosive mixed bacterial cultures (System 3), MS and Cu underwent severe corrosion of about 0.0817 and 0.0650 g, respectively. Compared to the control, both metals showed the higher WL in the presence of mixed culture (Raoa et al. 2000). Addition of corrosion inhibitor (System 2) resulted in an inhibition efficiency of about 81 and 90% for MS and Cu, respectively. In the presence of mixed cultures, however, the inhibition efficiency of the corrosion inhibitor was reduced about 25% (System 4). The addition of biocide (System 5) resulted in an inhibition efficiency of the MS and Cu at 56 and 50%, respectively. The use of both corrosion inhibitor and biocide (System 6) increased the corrosion inhibition efficiency of both metals to about 82 and 88%. When compared to the previous literature, higher corrosion inhibition efficiency was observed (Table 5). It can be concluded that the corrosion inhibitor adhesion on the metal surface increases the inactive film. The biocide inhibits the biofilm formation on MS and Cu metal surface. The growth pattern of bacterial culture with and without/inhibitor/biocide is shown in Fig S2. The growth rate of mixed culture in Cu and MS was noted as 10^4 and 10^5 . In contrast, the addition of inhibitor and biocide growth curve was significantly reduced up to 10^1 level due to inhibitor and biocide form a protective layer on the surface, and thus inhibit the bacterial

Table 4 Corrosion rate data for copper and mild steel in the presence/absence of mixed cultures/biocide/corrosion inhibitor (lab study)

System	Copper (g)				Mild steel (g)			
	Initial weight (W_o)	Final weight (W_f)	Weight loss (W_l)	Corrosion rate (mm/year)	Initial weight (W_o)	Final weight (W_f)	Weight loss (W_l)	Corrosion rate (mm/year)
1	5.0479	5.0406	0.0073	0.0177	6.1651	6.1075	0.0576	0.1589
2	5.0153	5.0108	0.0045	0.0109	5.7007	5.6895	0.0112	0.0309
3	5.011	4.946	0.065	0.1573	5.9188	5.8371	0.0817	0.2253
4	5.009	4.9847	0.0243	0.0588	5.5249	5.5037	0.0212	0.0585
5	5.0445	5.0235	0.021	0.0508	5.6174	5.5873	0.0301	0.0830
6	5.0433	5.0412	0.0021	0.0138	5.0455	5.0353	0.0102	0.0281

Table 5 Corrosion inhibition concentration of mild steel and copper in various environmental conditions

S. no.	Source of corrosion inhibitor/biocide	Concentration (ppm)	Metals used	Corrosion inhibition efficiency (%)	References
1	<i>Azadirachta indica</i> leaves extract	20	Mild steel	50	Shaily et al. (2014)
2	2- and 4-mercaptopyridines	20	Copper	63	Hassan and Holze (2009)
3	Watermelon rind extract	1000	Mild steel	54.33	Odewunmi et al. (2015)
4	<i>Kappaphycus alvarezii</i>	100	Mild steel	41.91	Kamal and Sethuraman (2013)
5	1-Hydroxyethylidene-1,1-diphosphonate	30	Copper	64	Rahmani et al. (2015)

attachment and growth. Generally, the addition of inhibitor and biocide system 6, the inhibitor/biocide was adsorbed on the Cu/MS metal surface as protective layer to prevent the biofilm formation and inhibit the adsorption corrosive chemical compounds, which leads to reduction of corrosion rate (Booth 1971; Narenkumar et al. 2017c).

Electrochemical study

Tafel polarization curve and its related data are presented in Fig S3 and Table 6 for Cu and MS metals in the presence and absence of the mixed cultures/inhibitor/biocide. The charge transfer resistance (R_{ct}) values of system 6 were higher in the presence of inhibitor and biocide ($8.21\text{E}+08$, $8.01\text{E}+07 \Omega \text{ cm}^2$) due to protective layer formed on the metal surface. In contrast, the presence of bacteria, creating the differential aeration/concentration cells, changing pH, depleting oxygen, utilizing cathodic hydrogen or by producing hydrogen, removing atoms from metals. Hence, the R_{ct} ($1.66\text{E}+04$ and $1.55\text{E}+03 \Omega \text{ cm}^2$) was significantly decreasing in the metal surface (system 3) (Flemming 1996). The open circuit potential (OCP) of mixed cultures was noted as

– 214 and – 198 mV, respectively. The mixed culture OCP was more negative, which indicated the breakdown of the protective film on the copper metal. Corrosion of iron in an aqueous environment was an electrochemical event that electrons engendered through anodic effect of metal and H^+ produced through dissociation of water. Combination of these reactions leads to molecular hydrogen formation. This process was called as cathodic polarization that a layer of hydrogen be able to shelter the metal. The key rust formed in this process is $\text{Fe}(\text{OH})_2$. The presence of inhibitor and biocide forms a layer on the metal surface and thus leads to the inhibition of hydrogen. In addition, the presence of inhibitor and biocide polarization curve was shifted to cathodic side (Zaravand and Ravishankar Rai 2016; Narenkumar et al. 2017a). The corrosion current (I_{corr}) increases in the mixed culture systems ($3.13 \times 10^{-6} \text{ A/cm}^2$) than control system ($2.06 \times 10^{-6} \text{ A/cm}^2$). Combination of corrosion inhibitor with biocide (System 6), led to a decrease in I_{corr} values for Cu and MS to about 6.78×10^{-7} and $2.02 \times 10^{-6} \text{ A/cm}^2$, when compared to control system. Hence, the corrosion inhibitor forms the protective passive film on MS and Cu metal surfaces which inhibited the bacterial attachment on

Table 6 Polarization and impedance data for copper and mild steel in the presence/absence of mixed cultures/biocide/corrosion inhibitor (lab study)

Systems	Metal	E_{corr} (mV)	Current density I_{corr} (A/cm^2)	B_a (V/dec)	B_c (V/dec)	Polarization resistance (R_p) ($\Omega \text{ cm}^2$)	Corrosion rate CR (mm/year)	Charge transfer resistance (R_{ct}) ($\Omega \text{ cm}^2$)
1	Cu	– 198	$2.06\text{E}-06$	0.128	0.399	$9.54\text{E}+03$	$3.05\text{E}-02$	$2.54\text{E}+05$
	MS	– 219	$3.69\text{E}-06$	0.122	0.354	$6.46\text{E}+03$	$4.34\text{E}-02$	$2.46\text{E}+04$
2	Cu	– 167	$8.66\text{E}-07$	0.139	0.609	$5.4\text{E}+04$	$8.91\text{E}-03$	$4.09\text{E}+06$
	MS	– 187	$1.97\text{E}-06$	0.180	0.278	$1.36\text{E}+03$	$2.32\text{E}-02$	$4.84\text{E}+05$
3	Cu	– 214	$3.13\text{E}-06$	0.135	0.373	$1.29\text{E}+04$	$2.19\text{E}-02$	$1.66\text{E}+04$
	MS	– 129	$5.65\text{E}-06$	0.104	0.272	$9.49\text{E}+03$	$1.94\text{E}-02$	$1.55\text{E}+03$
4	Cu	– 182	$3.69\text{E}-07$	0.149	0.337	$7.54\text{E}+04$	$3.80\text{E}-03$	$6.21\text{E}+06$
	MS	– 225	$1.49\text{E}-06$	0.130	0.344	$1.65\text{E}+04$	$1.75\text{E}-02$	$5.33\text{E}+06$
5	Cu	– 219	$2.21\text{E}-06$	0.134	0.437	$1.46\text{E}+04$	$2.26\text{E}-02$	$5.21\text{E}+05$
	MS	– 228	$1.99\text{E}-06$	0.39	0.366	$1.41\text{E}+04$	$2.34\text{E}-02$	$4.59\text{E}+05$
6	Cu	– 112	$6.78\text{E}-07$	0.259	0.619	$1.31\text{E}+05$	$6.97\text{E}-03$	$8.21\text{E}+08$
	MS	– 214	$2.02\text{E}-06$	0.153	0.503	$2.09\text{E}+04$	$2.37\text{E}-02$	$8.01\text{E}+07$

metal surface and thus control the MIC of both metals. The WL data confirmed the EIS data too (Rajasekar et al. 2005).

Surface analysis

The SEM image of the Cu and MS metal in the different systems is shown in Fig. 3. In the presence of mixed cultures, a thick biofilm was formed on Cu (Fig. 3a) and MS (Fig. 3a1) metal surfaces. The combination of the corrosion inhibitor with biocide resulted in significantly reducing the biofilm in both the metal surfaces. The biocide system showed the good antibacterial property against the corrosive bacteria in the cooling water environment.

The amount of corrosion caused by corrosive bacteria was assessed by pits on the coupon surface, using SEM analysis (Fig. 3). SEM analysis of the coupons after the end of the exposure time, the mixed bacterial culture in simulated cooling water environment showed severe pitting type of corrosion (Fig. 3b, b1) when compared to the control (Fig. 3a, a1). A significant reduction of mixed cultures on both the metals in the presence of biocide was evident in System 5. In contrast with System 1 and 3, no pitting type of corrosion was observed in the System 6.

FTIR analysis

The FTIR pattern of the biofilm formed on Cu and MS exposed to cooling water (System 1–6) is presented in Fig. 4. The narrow peaks observed in the range of 1000 cm^{-1} due to C–O group of polysaccharides. The band was obtained in the range of $3000\text{--}3500\text{ cm}^{-1}$ which was due to the presence of adsorbed water molecule and OH/NH groups (Fonseca et al. 2004; Jones and Amy 2000). The band at 1650 cm^{-1} corresponds to amide-I. A strong band observed as $1675\text{--}1620\text{ cm}^{-1}$ which assigned to the C=O stretching vibrations. The peak at $1242\text{--}1254\text{ cm}^{-1}$ stretching vibration was assigned to –OH group. The biofilms exhibited the high intensity of peaks in MS when compared to Cu, and showed that MS 1010 steel was very susceptible to biofilm formation. FTIR indicated that in the addition of corrosion inhibitor with biocide, the intensity of peaks was highly reduced, which was due to the lesser adhesion of mixed consortia on the metal samples (System 6).

Conclusion

The biocorrosion of metal surface (MS1010 and pure copper) exposure to the cooling water tower (field study) up to 90 days and simulated cooling water system (Lab study) was investigated successfully using weight loss method, EIS, FTIR and SEM–EDX analysis.

Field study

- Enumeration of total heterotrophic bacteria in cooling water sample collected from the cooling tower was found to be 2.12×10^4 CFU/mL. It confirms the presence of heterotrophic bacteria in the cooling water system.
- WL showed that MS 1010 has higher corrosion rate (0.2213 mm/year), when compared to the Cu metal (0.0116 mm/year) exposed to the cooling tower water (field study). The corrosion inhibitor forms an oxide layer on the metal surface and inhibits the corrosion reaction. It leads to the formation of compact biofilm-iron/copper oxide on the metal surface of MS 1010 and Cu. that layer disruption by accumulated corrosion products and thus inhibit the lesser compact biofilm-iron oxide/copper layer on the MS 1010 and Cu metal surface. EIS studies explained that cooling water contaminant (bacteria) accelerates the pitting corrosion of MS 1010 and Cu metal.
- SEM images reveal the biofilm formation in cooling tower water with exposure time. FTIR analyses confirmed that the organic and bacterial contaminants (MS and Cu) form a thick biofilm at the end of the 90 days of the immersion.

Lab study

- WL data for the simulated cooling water system in the lab study showed that the combination of the corrosion inhibitor and biocide resulted in an inhibition efficiency of about 82 and 88% in MS and Cu systems, respectively. Polarization studies showed that the presence of mixed cultures increased the corrosion current of Cu and MS 1010 to 3.13×10^{-6} and $5.6 \times 10^{-6}\text{ A/cm}^2$, respectively, compared to the control (2.06×10^{-6} and $3.69 \times 10^{-6}\text{ A/cm}^2$).
- SEM also confirms the antibacterial activity of the biocide on both the metal surfaces. FTIR results reveal that the EPS surface produced by the mixed culture covalently bound with the metal ion as Fe–O–C strong band on MS 1010 surface. The higher production of EPS on the MS and Cu metal surfaces thus increased the heterogeneity of the biofilm and caused differential aeration.
- MS surface was more susceptible to biocorrosion compared to Cu in cooling water environment, which was due to the high resistance of passive layer formation (copper oxide) on the copper surface.

This study concluded that the combined use of the corrosion inhibitor and biocide was effective inhibiting the biocorrosion of MS1010 and Cu in cooling water environment.

Fig. 3 SEM image of copper (**a**) and mild steel (**b**) coupons immersed in different systems in simulated cooling tower water. **a, a1** System 3, **b, b1** System 4, **c, c1** System 5 and **d, d1** System 6 (lab study)

Fig. 4 FTIR spectra of copper and mild steel samples in different systems in simulated cooling tower water (lab study) **a** copper, **b** mild steel

Compliance with ethical standards

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of interest The authors declare that they have no conflict of interest in the publication.

References

- Baars JK (1930) Over sulfaatreductie door bacteria in. Ph.D. thesis, University of Delft
- Beech IB, Gaylarde CC (1999) Recent advance in the study of biocorrosion—an overview. *Rev Microb* 30:177–190
- Booth GH (ed) (1971) Microbiological corrosion, M and B monographs CE11. Mills and Boon, London
- ColomboL A, Trasatt OSP (2018) Corrosion failure analysis of galvanized steel pipes in a closed water cooling system. *Eng Fail Anal* 84:46–58
- De la Fuente D, Diaz I, Simancas J, Chico B, Morcillo M (2011) Long term atmospheric corrosion of mild steel. *Corros Sci* 53:604–617
- El-Shamy AM, Soror TY, El-Dahan HA, Ghazy EA, Eweas AF (2009) Microbial corrosion inhibition of mild steel in salty water environment. *Mater Chem Phys* 114:156–159
- Flemming HC (1996) Economical and technical overview. In: Heitz E, Lemming H-C, Sand W (eds) Microbially influenced corrosion of materials. Springer, Heidelberg
- Fonseca ITE, Picciochi R, Mendonca MH, Ramos AC (2004) The atmospheric corrosion of copper at two sites in Portugal: a comparative study. *Corros Sci* 46:547–561
- Fontana MG (1986) Corrosion engineering. Mc-Graw Hill, New York
- Harrah T, Panilaitis B, Kaplan D (2004) Microbial exopolysaccharides. In: Dworkin M, Falkow S, Rosenberg E, Schleifer KH, Stackebrandt E (eds) The prokaryotes. Springer, New York, pp 88–115
- Hassan N, Holze R (2009) A comparative electrochemical study of electrosorbed 2- and 4-mercaptopyridines and their application as corrosion inhibitors at C60 steel. *J Chem Sci* 121:753–781
- Jayaraman A, Earthman JC, Wood TK (1997) Corrosion inhibition by aerobic biofilms on SAE 1018 steel. *Appl Microbiol Biotechnol* 52:267–275
- Jones DA, Amy PS (2000) Related electrochemical characteristics of microbial metabolism and iron corrosion. *Ind Eng Chem Res* 39:575–582
- Kamal C, Sethuraman MG (2013) *Kappaphycus alvarezii*—a marine red alga as a green inhibitor for acid corrosion of mild steel. *Mate Corros* 64:9999
- Ma Y, Li Y, Wang F (2000) Weatherability of 09CuPCrNi steel in tropical marine environment. *Corros Sci* 51:1725–1732
- MacDonald R, Brözel VS (2000) Community analysis of bacterial biofilms in a simulated recirculating cooling-water system by fluorescent in situ hybridization with rRNA-targeted oligonucleotide probes. *Water Res* 34:2439–2446
- Martinez SS, Gallegos AA, Martinez E (2004) Electrolytically generated silver and copper ions to treat cooling water: an environmentally friendly novel alternative. *Int J Hydrog Eng* 29:921–932
- NACE-RP0775 (2005) Standard recommended practice: preparation, installation, analysis, and interpretation of corrosion coupons in oilfield operations. NACE International, Houston, TX
- Narenkumar J, Madhavan J, Nicoletti M, Benelli G, Murugan K, Rajasekar A (2016) Role of bacterial plasmid on biofilm formation and its influence on corrosion of engineering materials. *J Bio Tribo Corros* 2:24
- Narenkumar J, Parthipan P, Nanthini AUR, Benelli G, Murugan K, Rajasekar A (2017a) Ginger extract as green biocide to control microbial corrosion of mild steel. *3 Biotech* 7:133. <https://doi.org/10.1007/s13205-017-0783-9>
- Narenkumar J, Sathishkumar K, Selvi A, Gobinath R, Murugan K, Rajasekar A (2017b) Role of calcium depositing bacteria *Agrobacterium tumefaciens* and its influence on corrosion of different engineering metals used in cooling water system. *3 Biotech* 7:374
- Narenkumar J, Parthipan P, Madhavan J, Murugan K, Suresh A, Rajasekar A (2017c) Bio-engineered silver nanoparticles: potent anti-corrosive inhibitor against corrosion of mild steel in cooling towers. *Environ Sci Pollut Res*. <https://doi.org/10.1007/s11356-017-0768-6>
- Narenkumar J, Ramesh N, Rajasekar A (2018) Control of corrosive bacterial community by biocide bronopol in industrial water system. *Biotech*. <https://doi.org/10.1007/s13205-017-1071-4>
- Obuekwe CO, Westlake DWS, Cook FD, Costerton JW (1981) Surface changes in mild steel coupons from the action of corrosion-causing bacteria. *Appl Environ Microbiol* 41:766
- Odewunmi NA, Umoren SA, Gasem ZM (2015) Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media *J Ind Eng Chem* 21:239–247
- Parthipan P, Ganesh Babu T, Anandkumar B, Rajasekar A (2017a) Biocorrosion and its impact on carbon steel API 5LX by *Bacillus subtilis* A1 and *Bacillus cereus* A4 isolated from crude oil reservoir, India. *J Bio Tribo Corros* 3:32. <https://doi.org/10.1007/s40735-017-0091-2>

- Parthipan P, Narenkumar J, Elumalai P, Preethi PS, Nanthini AUR, Agrawal A, Rajasekar A (2017b) Neem extract as a inhibitor for microbiologically influenced corrosion of carbon steel API 5LX in a hypersaline environments. *J Mol Liq* 240:121–127. <https://doi.org/10.1016/j.molliq.2017.05.059>
- Ping Xu (2012) MIC in circulating cooling water system. *Water Res* 4:203–206
- Rahmani K et al (2015) Evaluation of inhibitors and biocides on the corrosion, scaling and biofouling control of carbon steel and copper–nickel alloys. *Desalination*. <https://doi.org/10.1016/j.desal.2015.07.026>
- Rajasekar A, Ting YP (2011) Role of inorganic and organic medium in the corrosion behavior of *Bacillus megaterium* and *Pseudomonas* sp. in stainless steel SS 304. *Ind Eng Chem Res* 50:12534–12541
- Rajasekar A, Ting YP (2014) Characterization of corrosive bacterial consortia isolated from water in a cooling tower. *ISRN Corros* 10:1155
- Rajasekar A, Maruthamuthu S, Muthukumar N, Mohanan S, Subramanian P, Palaniswamy N (2005) Bacterial degradation of naphtha and its influence on corrosion. *Corros Sci* 47:257–271
- Rajasekar A, Ganesh Babu T, Karutha Pandian S, Maruthamuthu S, Palaniswamy N, Rajendran A (2007) Biodegradation and corrosion behaviour of manganese oxidizer *Bacillus cereus* ACE4 in diesel transporting pipeline. *Corros Sci* 49:2694–2710
- Rajasekar A, Maruthamuthu S, Ting YP (2008) Electrochemical behavior of *Serratia marcescens* ACE2 on carbon steel API 5L-X60 in organic/aqueous phase. *Ind Eng Chem Res* 47:7525–7532
- Rajasekar A, Xiao W, Sethuraman M, Parthipan P, Elumalai P (2017) Airborne microorganisms associated with corrosion of structural engineering materials. *Environ Sci Pollut Res*. <https://doi.org/10.1007/s11356-017-8501-z>
- Raoa TS, Sairam TN, Viswanathan B, Nair KVK (2000) Carbon steel corrosion by iron oxidising and sulphate reducing bacteria in a freshwater cooling system. *Corros Sci* 42:1417–1431
- Shaily M, Bhola A, Faisal M, Alabbas A, Rahul Bhola A, John R, Spear B, Brajendra Mishra A, David L, Olson A, Anthony E, Kakpovbia C (2014) Neem extract as an inhibitor for biocorrosion influenced by sulfate reducing bacteria: a preliminary investigation. *Eng Fail Anal* 36:92–103
- Shameer S (2016) Biosorption of lead, copper and cadmium using the extracellular polysaccharides (EPS) of *Bacillus* sp., from solar salterns. *3 Biotech* 6:194
- Wagner P, Little B (1993) Impact of alloying on microbiologically influenced corrosion a review. *Mater Perform* 32:65–68
- Wang Z, Fan Z, Xie L, Wang S (2006) Study of integrated membrane systems for the treatment of wastewater from cooling towers. *Desalination* 191:117–124.
- Wang J et al (2015) Hydroxyl carboxylate based non-phosphorus corrosion inhibition process for reclaimed water pipeline and downstream recirculating cooling water system. *J Environ Sci* 39:13–21
- Zarasvand KA, Ravishankar Rai V (2016) Identification of the traditional and non-traditional sulfate-reducing bacteria associated with corroded ship hull. *3 Biotech* 6:197