

Research on the application of compound microorganism preparation in reusing urban reclaimed water in circulating cooling water system

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ABSTRACT

A biological method was developed for reusing urban reclaimed water in circulating cooling water systems (CCWS), in which the compound microorganism preparation (CMP) mainly included nitrobacteria, *Bacillus subtilis*, photosynthetic bacteria and *Thiobacillus denitrificans*, was used to control the scaling, corrosion and biofouling of CCWS. The abundant carbon, nitrogen and phosphorus in urban reclaimed water met the needs of microbial growth. Compared with chemical agents, CMP had the advantages of high efficiency, no additional chemicals and being more economical. The research results showed that CMP improved water quality and decreased ammonia nitrogen ($\text{NH}_3\text{-N}$) and chemical oxygen demand (COD). The concentration ratio of CCWS reached 3.87 using CMP. The corrosion inhibition rate of CMP and the removal rate on biofouling achieved 99.69% and 22.21%, respectively. The mechanisms of CMP to control scaling, corrosion and biofouling were discussed, and the surface characteristics and chemical compositions of corrosion products and biofouling were analyzed.

Key words | biofouling, circulating cooling water system, compound microorganism preparation, corrosion, scaling, urban reclaimed water

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INTRODUCTION

Water resources are one of the most valuable non-renewable resources in the world. In recent years, water shortage has gained great worldwide attention and water reuse has become a focus in industrial enterprises such as power plants and chemical plants (Wang *et al.* 2016). Circulating cooling water is an indispensable water use in industry, and the water consumption and drainage amount account for 70–80% of the total industrial water (Ou *et al.* 2018). Therefore, research on water-saving technology of circulating cooling water in industry has great engineering application value.

Reclaimed water is a secondary-treated municipal wastewater effluent available in large quantities. Its water quality indicators are lower than drinking water, but higher than the permissible discharge standards of sewage. Urban reclaimed water has been regarded as the makeup water source of industry water (Wei *et al.* 2016; Jiao *et al.* 2017). However, the existing organic matter and high salinity of reclaimed

water can result in a series of problems, such as scaling, corrosion and biofouling in circulating cooling water systems (CCWS). These problems cause the deterioration of metallic surfaces and reduction of the efficiency of the heat exchanger (Tour *et al.* 2009; Liu *et al.* 2011). Research has shown that FeOOH is the main corrosion product of pipes, while CaCO_3 and $\text{Mg}_6\text{Al}_2\text{CO}_5\cdot(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ are the main components of pipe scale (Liu *et al.* 2014). In addition, appropriate temperature and pH in CCWS can promote microbial reproduction. Li *et al.* (2018) pointed out that microbes can switch to the utilization of elemental iron or other energetic metals as electron donors in an environment lacking carbon sources and other electron donors, leading to the corrosion of metals. Microorganisms are an important factor in the formation of biofouling. Some bacteria can produce adhesive extracellular polymeric substances (EPS), which are mostly composed of protein and polyose at levels of nearly 70–80% (Sponza 2002; Yu *et al.* 2012).

Chemical agents are some of the most commonly used materials in controlling scaling, corrosion and harmful microbe multiplication. Polyphosphates, zinc salt and organic phosphonic acid can be used as scale and corrosion inhibitors, and sodium hypochlorite is usually the biocide (Abd-El-Khalek & Abd-El-Nabey 2013). But the use of chemical agents may cause secondary pollution, and most of them are non-biodegradable. Su et al. (2014) found that the addition of biocide may promote the corrosion of carbon steel. Moreover, Zhang et al. (2016) reported that using phosphorous scale inhibitor increased calcium phosphate deposition in CCWS. Therefore, it is necessary to develop environmentally friendly corrosion and scale inhibitors to be used in CCWS.

Biological methods are a new treatment of circulating cooling water, which use compound microorganism preparations (CMP) to solve the problems of scaling, corrosion and biofouling. Compared with chemical treatment, biological treatment has excellent properties such as high efficiency, no additional chemicals and being more economical. At present, only a few studies about the application of biological method in scale and corrosion inhibition have been reported. Li et al. (2019) found that the soluble extracellular polymeric substances (s-EPS) secreted by *Bacillus cereus* could form a biomineralized film to inhibit corrosion and inhibit calcium scale crystal formation. Xiao et al. (2012) found that the corrosion resistance of 317 L stainless steel can be enhanced by nitrate produced by nitrification reactions of nitrobacteria. Qu et al. (2015) reported that *Bacillus subtilis* form a dense biofilm on the surface of cold rolled steel that slows corrosion. Moreover, some other studies showed that A2 amylase, trypsin, and cellulase have significant effects in inhibiting biofouling and no toxic substances are produced in CCWS by using enzyme treatment agents (Xu et al. 2012). The above research showed that the secretions of some microorganisms affect on

scale and corrosion inhibition. However, comprehensive evaluation for the application of biological methods in CCWS is still unclear. In fact, biological methods may be a promising way of reusing urban reclaimed water in CCWS since it contains abundant carbon, nitrogen and phosphorus elements, which are essential for microbial growth.

In this study, CMP as a biological treatment agent, with nitrobacteria, *Bacillus subtilis*, photosynthetic bacteria and *Thiobacillus denitrificans* were used to treat urban reclaimed water for reuse in CCWS. The scaling, corrosion and biofouling inhibition performance of CMP was evaluated by several methods. The change of pH, electrical conductivity, suspended solids, turbidity, ammonia nitrogen (NH₃-N), chemical oxygen demand (COD), limit concentration ratio and microbial community were all monitored in simulated circulating cooling water after adding CMP. The corrosion coupon experiment and biofouling culture experiment were conducted to compare the different corrosion rates of carbon steel and wet weights of biofouling with and without CMP. In addition, the mechanisms for corrosion, scaling and biofouling inhibition were discussed. The surface characteristics and chemical compositions of corrosion products and biofouling were analyzed.

MATERIALS AND METHODS

Characterization of the urban reclaimed water

The urban reclaimed water, a secondary-treated municipal wastewater effluent, was collected from North China Electric Power University Sewage Treatment Station in Baoding, China. The water quality index depended on temperature and other factors, and its characteristics are provided in Table 1.

Table 1 | Water quality index of the urban reclaimed water

Index	Value	Index	Value
pH	7.36–7.92	NH ₃ -N (mg/L)	2.76–5.98
Electrical conductivity (ms/cm)	0.62–0.74	COD (mg/L)	11.0–27.8
Suspended solids (mg/L)	3.04–7.77	Total phosphorus (mg/L)	3.52–3.82
Turbidity (NTU)	0.96–2.32	Dissolved oxygen (mg/L)	7.01–8.25
Color degree (CU)	32.90–36.12	Bacteria (10 ⁵ CFU/mL)	2.8–4.0
Total hardness (mmol/L)	1.60–2.30	Total alkalinity (mmol/L)	0.48–1.30
SO ₄ ²⁻ (mg/L)	61.44–81.36	Cl ⁻ (mg/L)	73.19–106.35
Ca ²⁺ (mg/L)	40–56	Mg ²⁺ (mg/L)	9.12–17.01

Ingredients of the compound microorganism preparation

In this experiment, the compound microorganism preparation (Beijing Hengjie Environmental Science and Technology Co., Ltd, China) was mainly composed of dry powder of nitrobacteria, *Bacillus subtilis*, photosynthetic bacteria and *Thiobacillus denitrificans*.

Experiment of microbial activation

Glucose, CMP and normal saline were mixed and heated by water bath to activate the microorganisms. Based on the principle that the suspension turbidity concentration of bacteria is proportional to the optical density (OD) value, the turbidimetric method was used to calculate the number of bacteria (Kolmert *et al.* 2000). The OD of the culture at 550 nm (OD_{550}) was measured over time using a photometer. In the experiment, OD_{550} and the corresponding culture time were used to determine the growth curve. All the experiments were performed in triplicate.

Simulation experiment of circulating cooling water

An analog system with necessary devices was used to evaluate the water improvement and scale inhibition performance of CMP. Figure 1 shows the main components and water direction of the analog CCWS.

In this experiment, the reclaimed water was used as the only makeup water source in the CCWS. The activated CMP, with a concentration of 200 mg/L, was added to the

water. The experimental temperature was $36 \pm 1^\circ\text{C}$ and the flow rate was 350 L/h. The water quality index was tested, covering pH, electrical conductivity, suspended solids, turbidity, $\text{NH}_3\text{-N}$, COD, total hardness and Cl^- .

ΔH is commonly used to evaluate the scale inhibition performance of reagents and to determine the limit concentration ratio in CCWS. When ΔH is less than 0.2, CCWS are in a state of metastability without scaling. When ΔH approaches 0.2, it is considered that CCWS were tending towards scaling, and the concentration ratio of the current system was the limit concentration ratio. The concentration ratio (Φ) and ΔH were calculated according to following formula:

$$\Delta H = \Phi_{\text{Cl}^-} - \Phi_{\text{YD}} = \frac{Cl_{\text{X}}^-}{Cl_{\text{B}}} - \frac{H_{\text{X}}}{H_{\text{B}}} \leq 0.2 \quad (1)$$

where:

ΔH is the difference between the concentration ratio of the chloride ions and total hardness;

Φ_{Cl^-} , Φ_{YD} are the concentration ratio of the chloride ions and total hardness;

Cl_{X}^- , Cl_{B} are the chloride ion values in circulating cooling water and supplementary water (mg/L);

H_{X} , H_{B} are the total hardness values in circulating cooling water and supplementary water (mmol/L).

In addition, the removal rate ($R\%$) of $\text{NH}_3\text{-N}$ or COD in experiment was calculated using the formula (2):

$$R(\%) = \frac{c_0 \times \Phi_{\text{Cl}^-} - c_{\text{x}}}{c_0 \times \Phi_{\text{Cl}^-}} \times 100 \quad (2)$$

where:

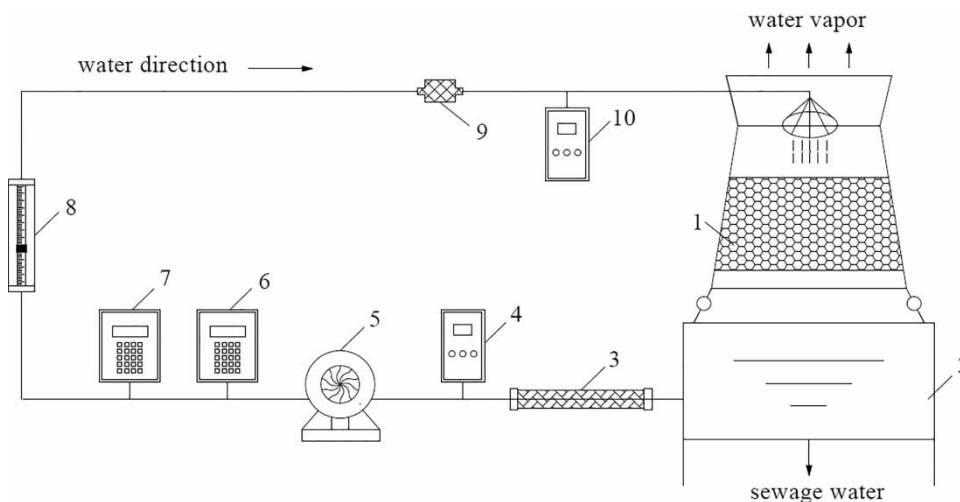


Figure 1 | Schematic representation of the analog CCWS. (1) cooling tower; (2) cooling tower basin; (3) temperature regulating device; (4) temperature probe; (5) circulating pump; (6) conductivity controller; (7) pH controller; (8) rotameter; (9) corrosion coupon; (10) temperature probe.

C_x is the $\text{NH}_3\text{-N}$ or COD value in recirculating cooling water (mg/L);

C_0 is the $\text{NH}_3\text{-N}$ or COD value in supplementary water (mg/L);

Φ_{Cl^-} is the concentration ratio of the chloride ion.

Monitoring of microbial community variation

The composition and variation of the microbial community in the circulating cooling water experiment were analyzed by high-throughput sequencing. Duplicate water samples were collected on day 1, day 14 and day 26. The procedures of DNA extraction, polymerase chain reaction (PCR) amplification and pyrosequencing were carried out as in previous studies (Cui et al. 2018; Lin et al. 2019; Ma et al. 2020). Relative abundances were based on the proportional frequencies of DNA sequences, to reflect the microbial community diversity.

Coupon experiment of corrosion

The corrosion rate was measured as the corrosion of a Q235 carbon steel coupon in reclaimed water with 200 mg/L CMP and without CMP added into beaker respectively; the concentration ratio of which was 2. Deionized water was used as supplementary water to keep the concentration ratio unchanged. Under the conditions of 36 °C and 100 r/min, the coupons were hung in the RCC-II rotary hanging-piece corrosion device. Three parallel samples were tested in each group, and the coupons were taken out of the device after 264 hours. The corrosion rate (F) and corrosion inhibition efficiency (η %) were calculated according to the standard of GB/T 18175-2014. The computational formulas were as follows:

$$F = \frac{C(w_0 - w)}{AT\rho} \quad (3)$$

$$\eta (\%) = \frac{F_0 - F_1}{F_0} \times 100 \quad (4)$$

where:

C is the conversion factor, 8.76×10^4 ;

w_0 , w are the weights of the coupon before and after corrosion (g);

A is the surface area of coupon (cm^2);

T is the corrosion time (h);

ρ is the density of the coupon materials (g/cm^3);

F_0 is the corrosion rate of the coupon without CMP (mm/a);

F_1 is the corrosion rate of the coupon with CMP (mm/a).

Culture experiment of biofouling

The biofouling formation was determined by the timing drain concentration method. Reclaimed water was used as timing drain concentration method inoculation solution and 200 mg/L CMP was added to one group but not the other group. Nutritional water was used as supplementary water to ensure adequate nutrients, i.e. $\text{C}_6\text{H}_{12}\text{O}_6$, $(\text{NH}_4)_2\text{SO}_4$, Na_2HPO_4 (C:N:P = 50:10:1) and tap water.

The beaker with hanging Q235 carbon steel coupon was put into the RCC-II rotary hanging-piece corrosion device, and the conditions were controlled at 36 °C and 100 r/min. Half of the water was discharged every 24 hours and nutritional water was added to the initial water level.

The coupons were taken out of the beaker every 24 hours, and the wet weight of biofouling was weighed after 5 min to eliminate the error of moisture. In order to reduce the error, three coupons were taken as parallel samples in each group. The wet weight of biofouling (M) and the removal rate (μ %) of CMP on biofouling are shown in Equations (5) and (6):

$$M = \frac{w_i - w_0}{A} \quad (5)$$

$$\mu (\%) = \frac{M_0 - M_1}{M_0} \times 100 \quad (6)$$

where:

w_i is the total wet weight of biofouling and the coupon (mg);

w_0 is the initial weight of the coupon (mg);

A is the surface area of the coupon (cm^2);

M_0 is the wet weight of biofouling without CMP (mg/cm^2);

M_1 is the wet weight of biofouling with CMP (mg/cm^2).

Surface analysis of corrosion products and biofouling

The surface characteristics and corrosion features of carbon steel coupons after the corrosion coupon experiment and circulating cooling water experiment were observed by scanning electronic microscopy (SEM). The corrosion products were scraped off the coupons using a sterile razor and the compositions were analyzed by energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD).

The coupons with biofouling were rinsed in normal saline and immersed in 4% glutaraldehyde solution for 24 hours to immobilize the biofouling. Then the biofouling was dehydrated successively with an ethanol gradient: 30%,

40%, 50%, 60%, 70%, 80%, 90%, and 100%. Finally, the biofouling was dried and tested using SEM, then detected using EDS and Fourier transform infrared spectroscopy (FT-IR) so as to help further confirm the chemical compositions.

RESULTS AND DISCUSSION

Microbial activation test

Figure S1 in the Supplementary Material shows the growth curve and pH change in the microbial activation phase. The OD value decreased slowly from 1 to 6 hours, indicating that the microorganisms were in the adaptive phase and growing slowly. The OD value increased rapidly from 6 to 9 hours and reached the peak value at 9 hours, which was 2.20 ± 0.13 , suggesting the microorganisms were in the

logarithmic phase. The OD value plateaued from 12 to 24 hours and at 12 hours was 1.41 ± 0.09 , showing that the microorganisms were in the stable growth phase. During the microbial activation, the pH value continued to decrease, ranging from 6.47 ± 0.08 to 4.12 ± 0.09 . The pH value was 4.43 ± 0.14 at 12 hours, after which thereafter the pH value tended to stabilize. In conclusion, 12 hours of microbial activation may be the best activation time, at which time the microorganisms are in the stable growth phase.

Water improvement and scale inhibition performance test

Figure 2 shows the change of water quality index in the circulating cooling water experiment. As shown in Figure 2(a), the concentration ratio increased steadily due to daily evaporation and supplement of reclaimed water. On days 14 and

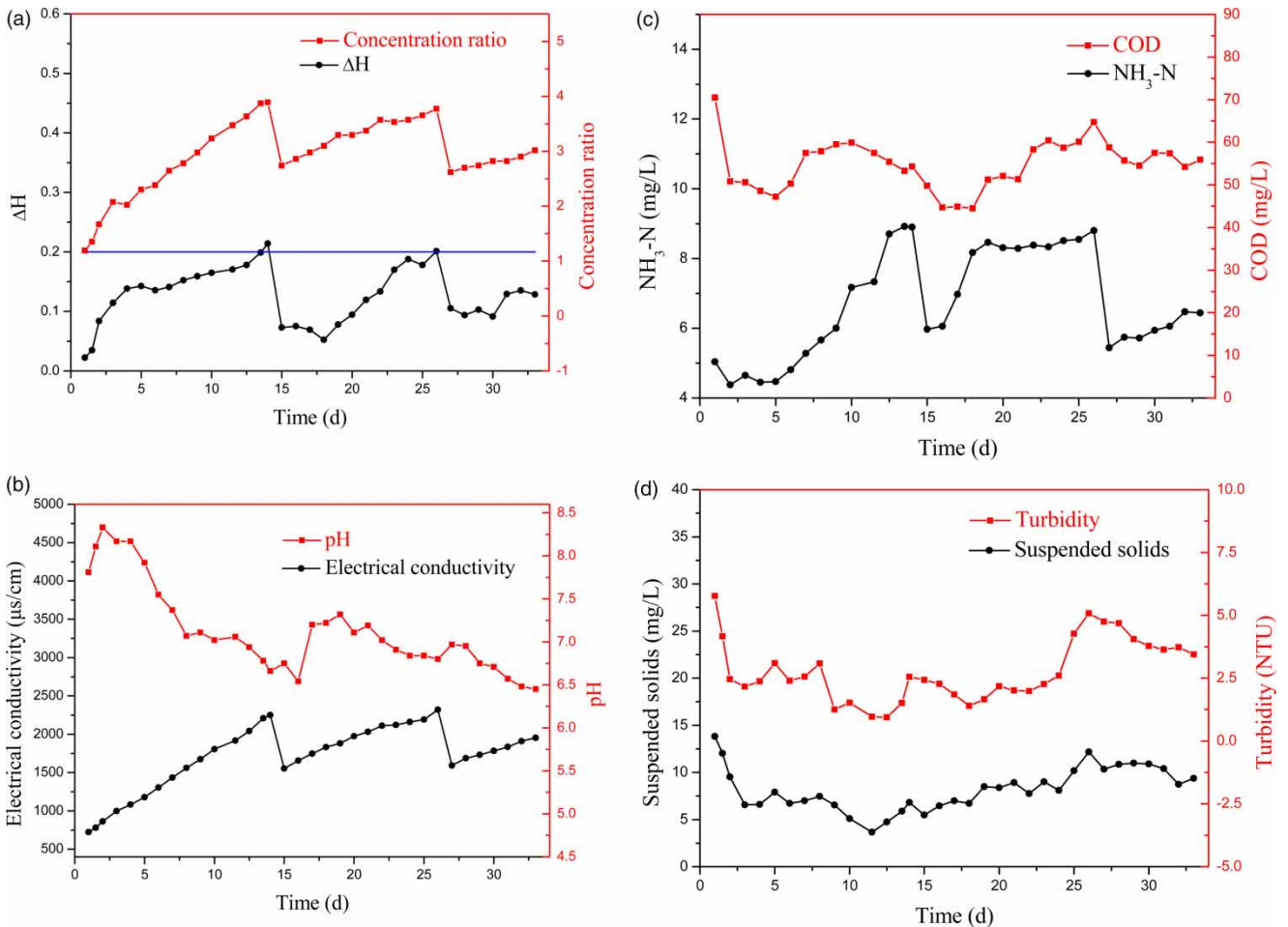


Figure 2 | The water quality index change of circulating cooling water experiment. (a) ΔH and concentration ratio change, (b) electrical conductivity and pH change, (c) $\text{NH}_3\text{-N}$ and COD change, (d) suspended solids and turbidity change.

26 of the experiment, ΔH exceeded the limit value of 0.2 and sewage discharge was carried out. The limit concentration ratio was 3.87 and the maximum Cl^- reached 347.41 mg/L, which was less than the maximum Cl^- limit (1,000 mg/L) of circulating cooling water standard. The schematic representation of scale inhibition mechanism by CMP is shown in Figure 3(a). The combination of H^+ produced by bacteria and CO_3^{2-} in water can become HCO_3^- . Because of the high solubility of $\text{Ca}(\text{HCO}_3)_2$, Ca^{2+} can be stable in water and without precipitation, thus achieving a scale inhibition effect. The concentration ratio of most power plants using general chemical treatment is only 2–3 in China (Ma et al. 2010b). Compared with chemical scale inhibitors, CMP achieves a higher concentration ratio.

The electrical conductivity of the experimental system increased steadily and reached the maximum of 2,320 $\mu\text{S}/\text{cm}$ (Figure 2(b)). The pH value showed an uptrend, with a peak of 8.33 at the beginning of the experiment. Thereafter the pH continued to decrease and the microflora was stable. The pH was 6.66 at the first sewage discharge, 6.80 at the second sewage discharge, and 6.45 at the lowest point of the system. This is because nitrobacteria can oxidize $\text{NH}_3\text{-N}$ to HNO_3 , which decreases the pH of system.

With the increase of concentration ratio, $\text{NH}_3\text{-N}$ increased slowly and reached a peak value of 8.92 mg/L (Figure 2(c)). According to the national regulations, the

$\text{NH}_3\text{-N}$ value of CCWS should not exceed 10 mg/L, and our experiment controlled it within this range. The highest removal rate of $\text{NH}_3\text{-N}$ was 55.57% in our experiment. This may be due to the fact that nitrobacteria, *Bacillus subtilis* and photosynthetic bacteria can degrade $\text{NH}_3\text{-N}$ (Fang Fang et al. 2010; Zhang et al. 2019). This is consistent with the experimental phenomenon of decrease in pH.

Due to the presence of organic substances such as glucose, COD increased rapidly after adding CMP. Thereafter, COD showed a downward trend, with a minimum of 44.5 mg/L and a maximum of 64.7 mg/L. According to the national regulations, the COD of CCWS should not exceed 100 mg/L. It was controlled within 60 mg/L in our experiment. The highest removal rate of COD was 29.03%. Photosynthetic bacteria can use organic substances, sulfides and ammonia in water as the hydrogen donor and carbon source for photosynthesis, thus removing COD (Wang & Zhen 2002).

There was no obvious fluctuation of turbidity and suspended solids in the circulating cooling water, which is shown in Figure 2(d). The highest turbidity value was 5.08 NTU and the lowest was 0.94 NTU. The maximum value of suspended solids was 12.19 mg/L and the minimum was 3.67 mg/L. The turbidity and suspended solids of the circulating cooling water were not increased significantly

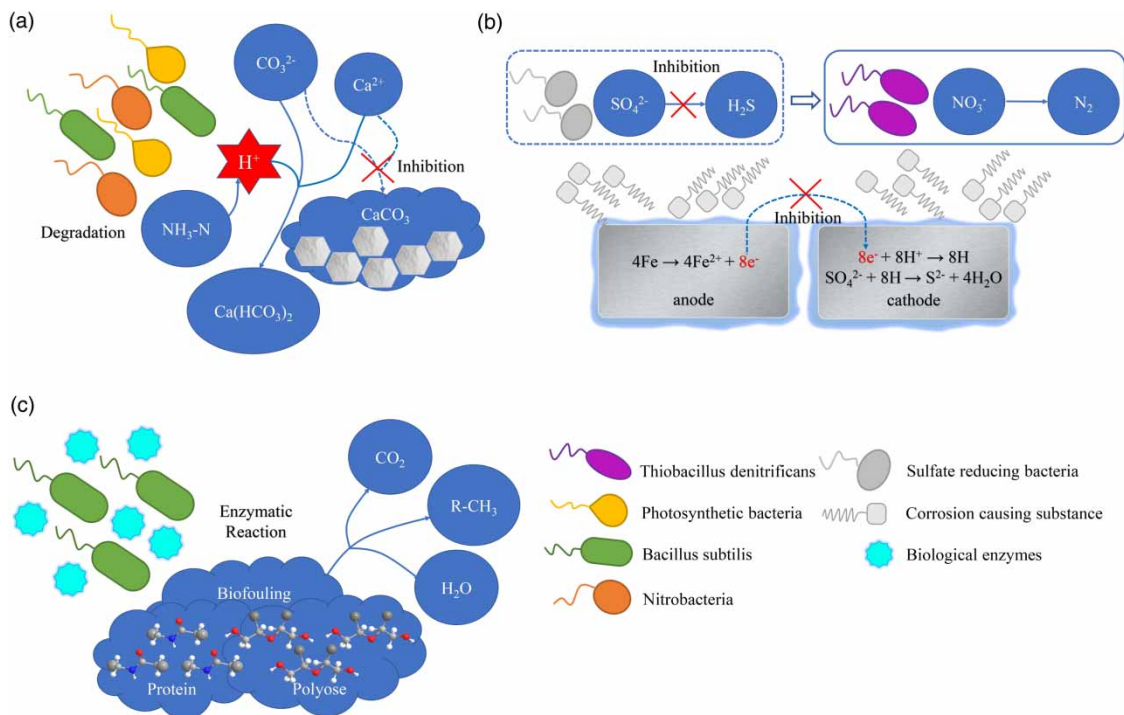


Figure 3 | Schematic representation of (a) scale inhibition (b) corrosion inhibition (c) biofouling inhibition mechanism by CMP.

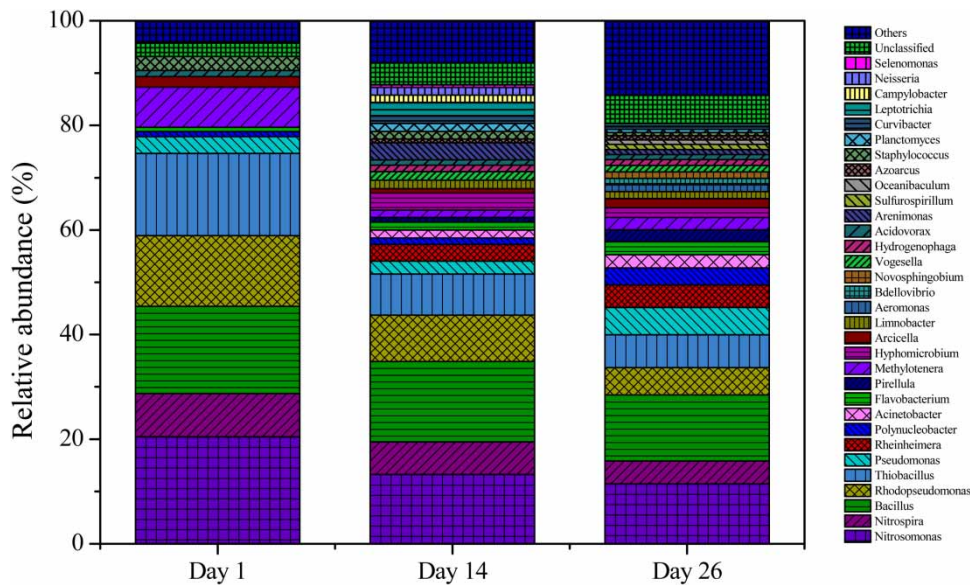


Figure 4 | Relative abundance of the main microorganisms at genus level in the circulating cooling water experiment. (Species whose relative abundance is less than 0.5% in all samples are merged into others.)

compared with the reclaimed water. This is because *Bacillus subtilis* play an important role in water quality improvement.

The relative abundance of the main microorganisms at genus level and the variation of functional strains in circulating cooling water experiment are shown in Figure 4. The functional strains included *Nitrosomonas* and *Nitrospira* (nitrobacteria), *Bacillus* (*Bacillus subtilis*), *Rhodospseudomonas* (photosynthetic bacteria) and *Thiobacillus* (*Thiobacillus denitrificans*). As the time went on, the structure of the microbial community in circulating cooling water changed significantly and became more complicated. The proportion of the functional strains in the microbial community were 74.64% (day 1), 51.57% (day 14) and 39.96% (day 26), respectively. When the system has been running for a long time, the functional strains are still dominant and play an active role. Compared with chemical agents, biological agents reduce the dosage and dosing frequency.

Corrosion inhibition performance test

In the corrosion coupon experiment, the surface of the coupon without CMP was obviously uneven and rough, while the coupon with CMP had a smooth surface and no corrosion phenomena. The SEM image shows that the porous structure of corrosion products emerged on the coupon surface when CMP was not added (Figure 5(a) and 5(b)). Furthermore, slight corrosion was observed on the

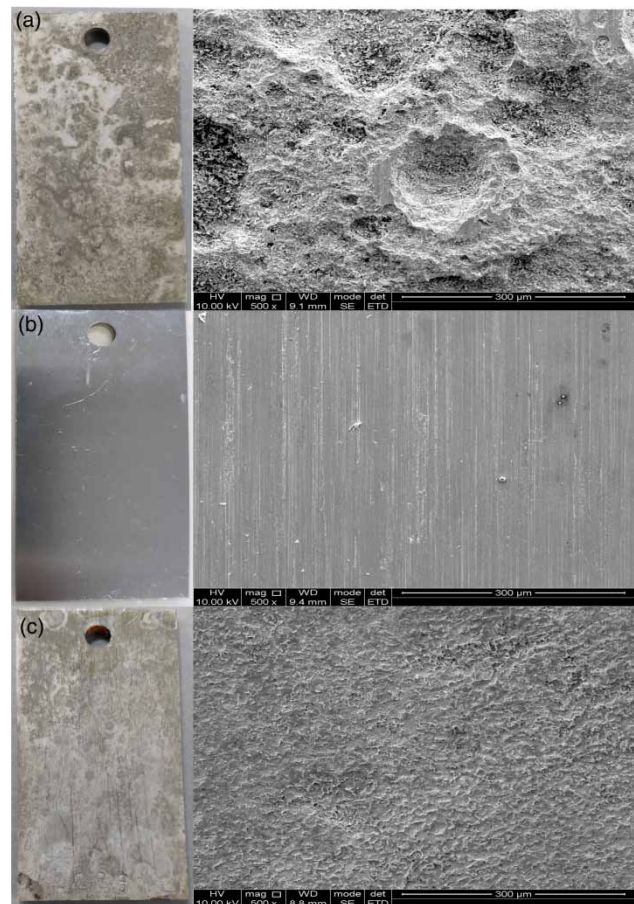


Figure 5 | The appearance and SEM images of carbon steel coupons in (a) the corrosion coupon experiment without CMP, (b) the corrosion coupon experiment with CMP and (c) the circulating cooling water experiment with CMP.

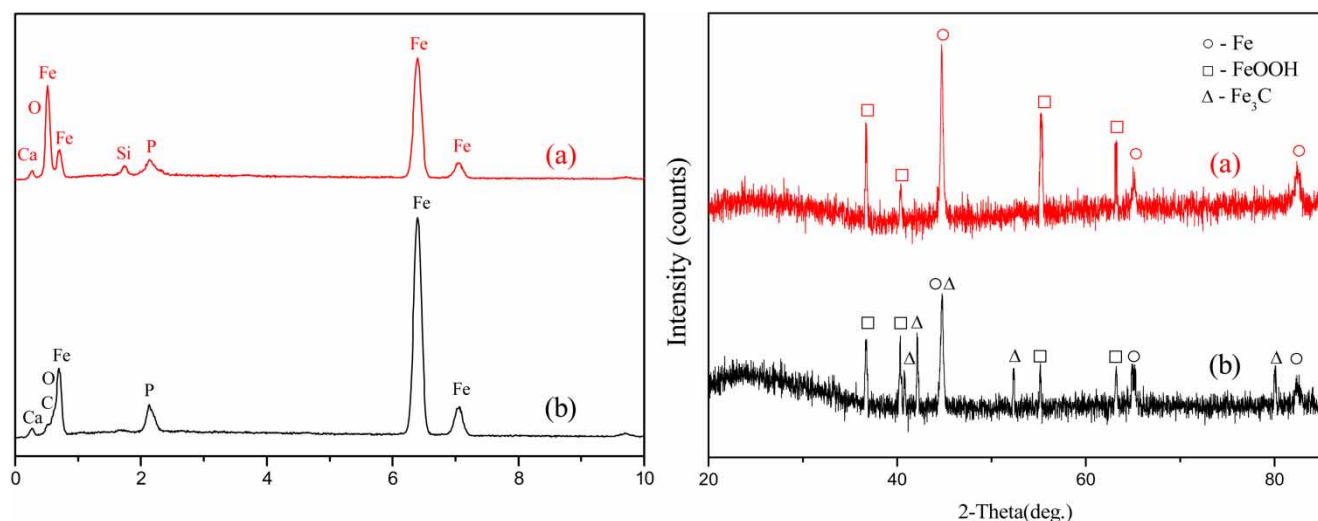


Figure 6 | EDS spectra and XRD pattern for corrosion products formed on carbon steel coupons in (a) the corrosion coupon experiment without CMP and (b) the circulating cooling water experiment with CMP.

coupon surface in the circulating cooling water experiment with CMP, but the corrosion degree was less than without CMP (Figure 5(c)). The corrosion products in the corrosion coupon experiment without CMP and the circulating cooling water experiment with CMP were analyzed (Figure 6). Along with elemental Fe, EDS qualitative analysis of the corrosion products revealed the presence of P, O, Si, C and Ca. XRD analysis further confirmed that the corrosion products were mainly FeOOH. In addition, Fe₃C was detected in the corrosion products from the circulating cooling water experiment with CMP.

Table 2 contains the detailed data of the coupon test. The average corrosion rate of carbon steel with CMP group was 0.0034 mm/a, which was far below the without

CMP group (1.0979 mm/a). The corrosion inhibition rate of CMP on carbon steel was 99.69%, which was higher than that of commonly used chemical corrosion inhibitor (Yongzhang *et al.* 2011). In addition, the average corrosion rate of carbon steel in the circulating cooling water experiment was 0.0654 mm/a. It was below the limit value of 0.0750 mm/a and reached the national standard.

The main reason for corrosion inhibition by CMP is that the microorganisms may form a layer of dense protective film on the metal surface (Figure 3(b)). Relevant studies have shown that the metabolic activity of the microorganisms forms a biofilm structure, which creates an effective scavenging system. It resists the threat of the environment and prevents the charge transfer between the anode and cathode (Eliana & Ausubel 2002; Beech & Sunner 2004; Videla & Herrera 2009; Suma *et al.* 2019). In addition, sulfate-reducing bacteria are important microorganisms for metal corrosion, as they produce sulfide to corrode metal (Kuang *et al.* 2007). *Thiobacillus denitrificans* in CMP can switch from sulfate reduction to nitrate reduction and inhibit the accumulation of sulfide, thus inhibiting corrosion (Garcia-de-Lomas *et al.* 2007; Alasvand Zarasvand & Rai 2014).

Biofouling inhibition performance test

Studies have shown that the growth process of biofouling is divided into three stages: initial attachment period, logarithmic growth period and stable attachment period (Little *et al.* 1986). As can be seen from Figure 7, the wet weight of biofouling remained constant 27 days later and the growth of

Table 2 | Corrosion rate of carbon steel coupon with and without CMP

Test	Serial number of coupon	Weightless value (g)	Corrosion rate (mm/a)	Average corrosion rate (mm/a)
Corrosion coupon experiment without CMP	1	0.7160	1.0809	1.0979
	2	0.7635	1.1526	
	3	0.7023	1.0602	
Corrosion coupon experiment with CMP	4	0.0014	0.0021	0.0034
	5	0.0028	0.0042	
	6	0.0026	0.0039	
Circulating cooling water experiment with CMP	7	0.1264	0.0636	0.0654
	8	0.1338	0.0673	
	9	0.1298	0.0653	

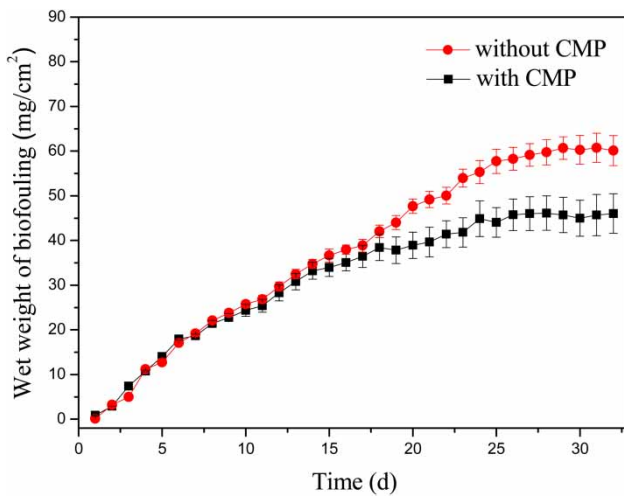


Figure 7 | Growth curve of biofouling with and without CMP.

biofouling reached the stable attachment period. The wet weight of biofouling with CMP was $46.02 \pm 3.76 \text{ mg/cm}^2$, while without CMP it was $59.16 \pm 2.53 \text{ mg/cm}^2$. The growth of aerobic, facultative and anaerobic microorganisms reached a stable state, and the growth and abscission of biofouling reached a balance in this period. The removal rate of CMP on biofouling reached 22.21% in our experiment. This was due to the existence of biological enzymes, which are mainly produced by *Bacillus subtilis* (Farzaneh *et al.* 2012). The mechanism of enzymatic reaction is shown in Figure 3(c). As a special catalytic protein, biological enzymes can act on complex chemical chains in biofouling and degrade them into small molecular organic matter or inorganic substances such as CO_2 and H_2O (Hui *et al.* 2018).

The surface of biofouling with CMP was smooth, while without CMP it was uneven and rough. Compared with without CMP, the SEM image of biofouling with CMP

showed a denser layer structure and low porosity (Figure 8). Related studies have demonstrated that biofouling with a layered structure makes the surrounding biofouling peel off together, which makes the removal effect on biofouling higher (Laopaiboon *et al.* 2003; Ma *et al.* 2010a). EDS and FT-IR spectra results showed that the compositions of biofouling were not significantly different in biofouling experiment with and without CMP. The characteristic elements of biofouling were Fe, P, O, C and Ca, and Fe mainly came from the carbon steel coupons. It could be seen from the FT-IR spectra that the characteristic absorption peaks of O-H/N-H bond and C=O bond stretching vibration appeared at the wave numbers of $3,430 \text{ cm}^{-1}$ and $1,633 \text{ cm}^{-1}$, respectively. The peaks at $1,402 \text{ cm}^{-1}$ and $1,122 \text{ cm}^{-1}$ might be due to the presence of $-\text{CH}_3$ and C-O (ester) bonds, respectively. Meanwhile, the flexural vibration absorption peak of C-H was observed at 562 cm^{-1} . The presence of these functional groups indicated that the protein and polyose were presented in biofouling, which were consistent with typical compositions of EPS (Wang *et al.* 2008). Moreover, it could be observed that the additional absorption peak of C-H appeared at 880 cm^{-1} and 794 cm^{-1} in Figure 8(b), indicating the organic substances were more complicated and varied in biofouling with CMP. This is because biological enzymes may degrade biofouling into some small molecular organic substances.

CONCLUSIONS

CMP as a biological treatment agent was used for the reuse of urban reclaimed water in CCWS and to solve the problems of scaling, corrosion and biofouling through microbial metabolism. CMP was activated for 12 hours to achieve optimum operating conditions. The research results

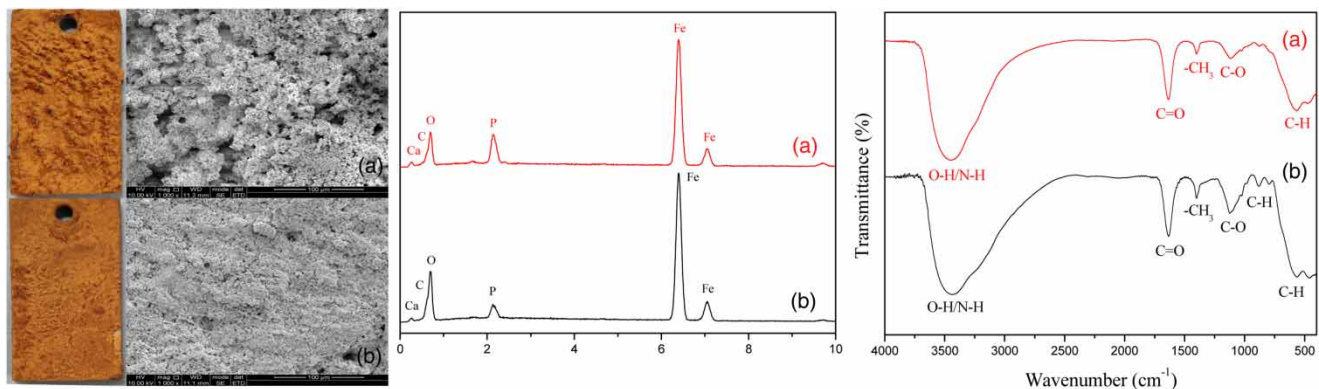


Figure 8 | SEM images, EDS spectra and FT-IR spectra of biofouling in the biofouling culture experiment (a) without CMP and (b) with CMP.

showed that CMP improved water quality and decreased $\text{NH}_3\text{-N}$ by the metabolism of nitrobacteria and *Bacillus subtilis*. Photosynthetic bacteria could use organic substances, sulfides and ammonia as the hydrogen donor and carbon source for photosynthesis, there by achieving the removal of COD. In this experiment, the concentration ratio in CCWS reached 3.87. Because CO_3^{2-} in water became HCO_3^- by bacterial action, carbonate was stable in water and there was no scaling. The formation of biofilm and the inhibition of sulfide slowed the metal corrosion, and the corrosion inhibition rate of CMP reached 99.69%. The removal rate of CMP on biofouling reached 22.21%, which was mainly caused by biological enzymes. They acted on complex chemical chains in biofouling and degrade them. EDS/XRD analyses confirmed that FeOOH was the main component of the corrosion products, and EDS/FT-IR spectra indicated that biofouling was composed protein and polyose.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at <https://dx.doi.org/10.2166/wst.2019.430>.

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