Inhibition effect of phosphorus-based chemicals on corrosion of carbon steel in secondary-treated municipal wastewater
Zhanhui Shen, Hongqiang Ren, Ke Xu, Jinju Geng and Lili Ding

ABSTRACT
Secondary-treated municipal wastewater (MWW) could supply a viable alternative water resource for cooling water systems. Inorganic salts in the concentrated cooling water pose a great challenge to corrosion control chemicals. In this study, the inhibition effect of 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), trimethylene phosphonic acid (ATMP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) on corrosion of carbon steel in secondary-treated MWW was investigated by the means of potentiodynamic polarization and electrochemical impedance spectroscopy. The inhibition effect increased with increasing concentration of inhibitors. The corrosion rates of carbon steel were 1.5, 0.8, 0.2 and 0.5 mm a\(^{-1}\) for blank, HEDP, ATMP and PBTCA samples at 50 mg L\(^{-1}\), respectively. The phosphorus-based chemicals could adsorb onto the surface of the carbon steel electrode, form a coat of protective film and then protect the carbon steel from corrosion in the test solution.

INTRODUCTION
Secondary-treated municipal wastewater (MWW) could provide a viable alternative source to freshwater for industrial cooling water systems (Wade Miller 2006; Vidic 2009; Li et al. 2011). Secondary-treated MWW usually contains appreciable amounts of hardness, ammonia, phosphate, dissolved total solids and organic matter compared to fresh water (Weinberger 1966; Williams & Middlebrooks 1982). However, the low quality of the secondary-treated MWW presents challenges for the cooling plants in the form of mineral scaling and metal corrosion.

For cooling water systems, electrochemical technology including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) is commonly used to investigate the inhibition effect of corrosion inhibitors.

Marín-Cruz et al. (2006) studied the carbon steel/cooling water interface in synthetic test solutions using EIS. Results showed that hydroxyphosphonoacetic acid and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) could chelate with Ca\(^{2+}\) and generate a layer that provides good protection against corrosion. Naderi & Attar (2009) reported zinc aluminum polyphosphate and strontium aluminum polyphosphate showed greater inhibitive properties than conventional zinc phosphate in 3.5% w/w NaCl aqueous solution, due to the formation of a layer on the sample surface. Monosaccharide derivatives were studied as corrosion inhibitors in synthetic solutions; results demonstrated a high inhibition efficiency and showed that MoO\(_4^{2-}\) could enhance the inhibition efficiency (Touir et al. 2009). Abdel-Gaber et al. (2011) extracted organic matter from olive leaves, which they demonstrated to be efficient as a corrosion inhibitor for carbon steel under test condition. Sodium gluconate was used as corrosion inhibitor and showed great corrosion inhibition efficiency, even in an aggressive medium such as 3% NaCl solution (Touir et al. in press). Yuce & Kardas (2012) reported how 2-thiohydantoin acted as a mixed-type inhibitor by simultaneously suppressing the cathodic and anodic processes via physical adsorption on the carbon steel surface obeying the Langmuir adsorption isotherm. Mahgoub et al. (2010) used heterocyclic compounds as a corrosion inhibitor, and investigated the...
inhibition effect for carbon steel and stainless steel in stagnant cooling water. The tolyl compound serves as a multipurpose inhibitor that can suppress the uniform corrosion of carbon steel and pitting corrosion of stainless steel.

To date, most research has focused on the inhibition effect of chemicals in synthesized solution or simulated solution or acid solution. Few publications describing the inhibition efficiency of chemicals in real secondary-treated MWW solution could be found.

Within certain kinds of corrosion inhibitors, phosphorus-based chemicals are usually used in recycling cooling water systems to control mineral scaling and metal corrosion (Wijesinghe et al. 1996; Zhang et al. 2008; Hsieh et al. 2010; Li et al. 2011). HEDP and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) at a dosage of 10 mg L\(^{-1}\) was not efficient in controlling carbon steel corrosion when using a secondary-treated MWW alternative make-up water for cooling tower systems (Hsieh et al. 2010). However, at a dosage of 40 mg L\(^{-1}\), HEDP, PBTCA and trimethylene phosphonic acid (ATMP) showed high corrosion inhibition efficiency for carbon steel when using pre-treated coking wastewater as the make-up water for cooling water systems (Zhang et al. 2008).

In this study, the secondary-treated MWW was collected from Nanjing Chengbei wastewater treatment plant and used as test solution. The corrosion inhibition effect of HEDP, PBTCA and ATMP at different concentration was investigated using potentiodynamic polarization and EIS. The mechanism was discussed based on the fitting results according to the electrical equivalent circuit.

**METHODS**

**Test solution**

The secondary-treated MWW effluent was collected from the Chengbei wastewater treatment plant located in Nanjing, China (32.105 N, 118.750 E), for which the anaerobic/anoxic/oxic integrated active sludge process is adopted. The water quality data are provided in Table 1. HEDP, ATMP and PBTCA were used as corrosion inhibitors, all of which were supplied by Nanjing Naco Water Treatment Technology Co, Ltd.

**Preparation of electrodes**

All the electrochemical tests were carried out with a CS310 electrochemical test system (Wuhan Corrtest Instrument Co. Ltd, China). A three-electrode arrangement was employed with the 20# carbon steel sample as the working electrode (WE), the KCl-saturated calomel electrode (SCE) as the reference electrode and the platinum electrode as the counter electrode. The composition (wt%) of the 20# carbon steel was: C 0.18; Si 0.19; Mn 0.42; P 0.03; S 0.03; Ni 0.25; Cr 0.25; Cu 0.25 and the rest was Fe. The WE was prepared by using epoxy resin with an exposure active surface area of 0.5 cm\(^2\). Before each experiment, the WE was ground using emery paper to a 1,200 grit surface finish. Specimens were then washed with deionized water, acetone and deionized water, respectively.

**Electrochemical tests**

The three-electrode cell was kept at 40 °C (±0.5 °C) in a water bath. Prior to tests, a stabilization time of 120 min was applied to obtain a stable open circuit potential. The EIS experiments were conducted in the frequency range 100 kHz–0.01 Hz at the open circuit potential by applying an alternating current signal of 10 mV peak-to-peak. Each polarization scan was performed from -10 to 10 mV with respect to the stable open circuit potential at a scan rate of 0.5 mV s\(^{-1}\).

**Table 1 | Chemical composition of the secondary-treated MWW**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Si</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>SO(_4^{2-})</th>
<th>Cl(^-)</th>
<th>COD</th>
<th>TP</th>
<th>TN</th>
<th>N-NH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount present (mg L(^{-1}))</td>
<td>6.25</td>
<td>53.0</td>
<td>10.1</td>
<td>11.3</td>
<td>40.2</td>
<td>96.1</td>
<td>701.2</td>
<td>53.4</td>
<td>0.14</td>
<td>12.0</td>
<td>0.45</td>
</tr>
<tr>
<td>Total alkalinity (mmol L(^{-1}))</td>
<td>2.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.1</td>
</tr>
<tr>
<td>Conductivity (µS cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>626</td>
</tr>
</tbody>
</table>

COD: chemical oxygen demand; TP: total phosphorus; TN: total nitrogen.
RESULTS AND DISCUSSION

Corrosion inhibition effect of HEDP, ATMP and PBTCA on carbon steel

The corrosion rate of carbon steel in secondary-treated MWW was investigated at 40°C with or without adding phosphorus-based chemicals by using the potentiodynamic polarization. The potentiodynamic polarization curve was obtained through a polarization scan by using a CS310 electrochemical test system (Wuhan Corrtest Instrument Co. Ltd, China). Polarization resistance, $R_p$, fitting was carried out based on the polarization curve to obtain the corrosion rate of the test system (Figure 1). For the blank sample, the corrosion rate was about 1.5 mm a$^{-1}$. Within the range 10–50 mg L$^{-1}$, the corrosion rate decreased with increasing concentration of inhibitors. This may be due to an increase in the number of molecules adsorbed over the steel surface, blocking the active sites of acid attack and thereby protecting the metal from corrosion (Quraishi et al. 2010; Behpour et al. 2011; Soltani et al. 2012).

For all three phosphorus-based corrosion inhibitors (HEDP, ATMP and PBTCA) at concentrations of 10 mg L$^{-1}$, no corrosion inhibition effect was apparent. These results were in accordance with previous research works (Wijesinghe et al. 1996; Zhang et al. 2008). However, when the concentration of inhibitors was increased to 40 mg L$^{-1}$, the inhibition effect was visible. At a concentration of 50 mg L$^{-1}$, ATMP could control the corrosion rate of carbon steel in secondary-treated MWW to <0.2 mm a$^{-1}$. In contrast with the blank sample, ATMP showed excellent corrosion inhibition efficiency (>90%). With the increase of HEDP concentration from 10 to 50 mg L$^{-1}$, the corrosion rate decreased gradually to 0.8 mm a$^{-1}$. For PBTCA, a similar trend of corrosion rate was observed. The corrosion rate was about 0.5 mm a$^{-1}$ in the presence of 50 mg L$^{-1}$ PBTCA. At a dosage of 50 mg L$^{-1}$, HEDP, ATMP and PBTCA (especially ATMP) could control the corrosion of carbon steel in secondary-treated MWW at 40°C. The order of the corrosion inhibition effect was ATMP > PBTCA > HEDP.

Potentiodynamic polarization plots

The potentiodynamic polarization plots of carbon steel in the secondary-treated MWW at different concentration of inhibitors are depicted in Figure 2. In the test solution, the anodic reaction of corrosion is the passage of metal ions from the metal surface in the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen. The inhibitor could affect either the anodic or the cathodic reaction or both (Kosari et al. 2011). The displayed plots show that the addition of phosphorus-based corrosion inhibitor shifted the corrosion potential to less negative values and decreased the corrosion current density.

For all three phosphorus-based inhibitors, increasing the concentration of inhibitor could enhance the inhibition effect. Low concentrations (10 mg L$^{-1}$) could not affect the potentiodynamic polarization plots significantly, which was in agreement with previous research (Wijesinghe et al. 1996; Zhang et al. 2008). However, when the inhibitor concentration increased to 40 or 50 mg L$^{-1}$, the potentiodynamic polarization plots changed markedly in contrast with blank samples. ATMP demonstrated greater effect than HEDP and PBTCA on the potentiodynamic polarization plots on carbon steel. In the presence of ATMP (50 mg L$^{-1}$), the corrosion potential was shifted from 0.49 mV to about 0.23 mV of the blank sample and the corrosion current density decreased to $10^{-8}$ A cm$^{-2}$ (Figure 2(b)). For HEDP and PBTCA, the corrosion potential was shifted to about 0.52 and 0.30 mV respectively and the corrosion current density decreased to some extent (Figure 2(a), (c)).

Electrochemical impedance spectroscopy

To provide further information on the corrosion inhibition effect of the phosphorus-based chemical, EIS tests were carried out. Using Zview software, we fitted the test results based on the electrical equivalent circuit shown in Figure 3. The fitting parameters and results are listed in Table 2.
Figure 2 | Polarization plots of carbon steel in secondary-treated municipal wastewater in the presence of (a) HEDP; (b) ATMP; or (c) PBTCA.

Figure 3 | The electrical equivalent circuit and (a) Nyquist; (b) Bode; and (c) phase angle plots. (Z, Z₀ and Z₀₀ are electrical impedance, real part of electrical impedance and imaginary part of electrical impedance, respectively.)
The relationship between electrochemical impedance (Z) and electrical elements under the test situation is defined:

\[
Z = R_s + \frac{1}{j\omega C_F} + \frac{1}{R_c} + \frac{1}{j\omega C_{dl}} + \frac{1}{R_t} + \frac{1}{Z_w}
\]

where \( R_s \) is the solution resistance; \( j \) is \( \sqrt{-1} \); \( \omega \) is angular frequency; \( C_F \) is the film capacitance; \( R_c \) is the film resistance; \( C_{dl} \) is the double-layer capacitance; \( R_t \) is the charge transfer resistance; and \( Z_w \) is Warburg’s impedance. As shown in Figure 3, six electrical elements were used in the electrical equivalent circuit to fit the impedance spectra.

In the presence of inhibitors, the film resistance and the charge transfer resistance of the test samples was much higher than that of the blank sample, especially for ATMP. As shown in Table 2, the film resistance and the charge transfer resistance was 260.2 and 269.1 \( \Omega \) cm\(^2\) respectively in the absence of inhibitors. In the presence of ATMP, the film resistance and the charge transfer resistance was 892.4 and 1,735 \( \Omega \) cm\(^2\) respectively. This may be due to the formation of a protective film on the surface of the carbon steel electrode. The film resistance and the charge transfer resistance increased because of the protective film. The three phosphorus inhibitors could control the corrosion of carbon steel by forming a protective film on the metal surface in the secondary-treated MWW solution. Additionally, the chi-squared test results revealed that the model calculation and prediction showed good agreement with the experimental results (\( p < 0.01 \)).

Table 2 | The fitting parameters of electrochemical impedance spectroscopy tests (\( T, P \) and \( R \) are temperature, polarization and resistance factors)

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>( R_s ) (( \Omega ) cm(^2))</th>
<th>( R_t ) (( \Omega ) cm(^2))</th>
<th>( C_F \times 10^{-4} )</th>
<th>( C_{dl} \times 10^{-4} )</th>
<th>( C_r \times 10^{-4} )</th>
<th>( Z_w-T )</th>
<th>( Z_w-P )</th>
<th>Chi-squared (&lt; 0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>36.44</td>
<td>260.2</td>
<td>7.646</td>
<td>0.7432</td>
<td>269.1</td>
<td>310.7</td>
<td>0.6201</td>
<td>1,742</td>
</tr>
<tr>
<td>HEDP</td>
<td>63.37</td>
<td>291.2</td>
<td>6.063</td>
<td>0.9083</td>
<td>694.4</td>
<td>11.94</td>
<td>0.6129</td>
<td>239.8</td>
</tr>
<tr>
<td>ATMP</td>
<td>40.84</td>
<td>892.4</td>
<td>2.447</td>
<td>0.9368</td>
<td>1,735</td>
<td>6.704</td>
<td>0.8882</td>
<td>939.1</td>
</tr>
<tr>
<td>PBTC A</td>
<td>43.40</td>
<td>316.1</td>
<td>3.522</td>
<td>0.9291</td>
<td>568.2</td>
<td>9.456</td>
<td>0.8322</td>
<td>495.5</td>
</tr>
</tbody>
</table>

In the presence of a corrosion inhibitor, the imaginary part of the impedance also increased markedly. The radius of the semicircle became larger in the presence of inhibitor in contrast to the blank sample. In the low-frequency range, the charge transfer resistance and film resistance dominated the impedance. Inhibitors could be adsorbed onto the carbon steel surface and form a protective film; the transfer resistance and the film resistance then increased significantly. As a result, the corrosion rate of carbon steel was controlled.

Among the three phosphorus-based corrosion inhibitors, ATMP showed the best ability to control carbon steel corrosion, which showed agreement with the observed \( R_p \) results. Both amino groups and phosphate groups of ATMP could react with the carbon steel surface, which may contribute to the formation of protective film on the surface.

The impedance modulus in the low-frequency range could be used to compare the corrosion resistance of different samples. A larger impedance modulus demonstrates better corrosion protection. The three phosphorus-based corrosion inhibitors demonstrated a large inhibition effect on carbon steel corrosion. The order of the corrosion inhibition effect was ATMP > PBTC A > HEDP, which agreed with the experimental \( R_p \) results. Otherwise, the predicted curves were a good match to the observed data. In the presence of an inhibitor, the phase angle (0.1–1,000 Hz) curve when plotted against frequency was wider and of higher value in contrast to the blank sample, which could be attributed to the protective film formation of phosphorus-based chemicals on the carbon steel surface. In the presence of ATMP, the phase angle increased to 70 degrees; the negative value indicated the superior corrosion inhibition behavior due to the adsorption of ATMP onto the carbon steel surface.
CONCLUSIONS

HEDP, ATMP and PBTC showed a very good corrosion inhibition effect on carbon steel in secondary-treated MWW at 40 °C. The order of the inhibition effect was ATMP > PBTC > HEDP. The three phosphorus-based chemicals shifted the corrosion potential to less negative values and decreased the corrosion current density. The EIS data were well fitted based on the electrical equivalent circuit by using Zview software. The three phosphorus-based corrosion inhibitors were adsorbed onto the surface of the carbon steel electrode and formed a protective film coating, which protected the carbon steel from corrosion. ATMP showed a better inhibition effect than the other two, which may be due to the amino groups and phosphate groups of ATMP.

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REFERENCES


