Inhibition effect of dissolved organic matter in secondary-treated municipal wastewater on corrosion of N80 carbon steel

Zhanhui Shen, Shuzhan Zhang, Xingyi Dong, Jialu Shi, Jing Fan and JianSheng Li

ABSTRACT

Secondary-treated municipal wastewater (MWW) is the alternative water source in recirculating cooling water systems. Municipal wastewater treatment plant (WWTP) effluent was collected and four fractions including hydrophobic acidic (HPOA), hydrophobic alkaline (HPOB), weakly hydrophobic (WHPO) and hydrophilic (HPI) organics were isolated from the effluent by using DAX-8/XAD-4 resin. We used potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) to investigate corrosion characteristics of N80 carbon steel in the different water samples and control samples. In contrast with control samples, the corrosion rate of N80 carbon steel decreased 41%, 23%, 18% and 4% in the presence of HPOA, HPOB, WHPO and HPI, respectively. The results were further confirmed by the EIS test. In the presence of the four fractions (especially HPOA), the radius of the semicircle in the Nyquist plot was much larger than that for the control samples, which indicated that the impedance in the EIS test of the HPOA sample was much higher than that of the control sample. The dissolved organic matter (DOM) could adsorb onto the surface of the electrode and form a protective film, which could inhibit electron transfer and increase the electrochemical impedance of the electrochemical test system.

Key words | carbon steel, corrosion, municipal wastewater, organic matter

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INTRODUCTION

Water used in cooling water systems accounts for the major part of industrial water consumption. With the increasing shortage of water resources, secondary-treated municipal wastewater (MWW) could provide a viable alternative source to freshwater for industrial cooling water systems (Wade Miller 2006; EPRI 2008; Vidic & Dzombak 2009; Li et al. 2011). However, secondary-treated MWW usually contains appreciable amounts of hardness, ammonia, phosphate, total solids and dissolved organic matter (DOM) compared with freshwater (Weinberger et al. 1966; Williams 1982), which poses a great challenge to the cooling plants, because of mineral scaling and metal corrosion.

Organic matter such as humic matter, carbohydrate, protein and nucleic acid could be detected in the secondary-treated MWW (Ni et al. 2010; Vakondios et al. 2014), which showed potential effects on metal corrosion of cooling water systems when using secondary-treated MWW as make-up water. In tertiary-treated MWW, pH, ammonia, and organic matter were identified as important corrosion-influencing parameters. However, corrosion of mild steel and copper alloys could be controlled within acceptable limits using the corrosion inhibitor tolyltriazole (Choudhury et al. 2012). Another study showed microbial and corrosive risk would be increased when the system is replenished by municipal reclaimed water instead of surface water (Ping et al. 2015).

DOM in water negatively affects copper corrosion protection of drinking water pipelines (Edwards & Sprague

2001). Researchers investigated the influence of organic matter on copper and mild steel corrosion by using sodium acetate or glucose to prepare synthetic secondary-treated MWW or river water. Both glucose and sodium acetate had little influence on the overall corrosion of mild steel (Choudhury *et al.* 2012; Choudhury *et al.* 2016). Natural organic matter (NOM) could decrease the iron corrosion rate in drinking water pipelines due to surface complexation (Elfström Broo *et al.* 1999). The organic matter in sea water could associate with the corrosion products of mild steel which may play an important role in influencing the corrosion of mild steel in these tropical marine waters (Bhosle & Wagh 1992). Some previous research focused on the effect of organic matter in synthetic water on corrosion of metal. Others focused on the effect of organic matter coexisting with other pollutants in the water on corrosion of metal. However, DOM in the secondary-treated MWW could be separated and concentrated in order to actually investigate the effect of DOM itself on corrosion of cooling system metals.

DOM of surface water or wastewater could be divided into hydrophobic acid, base and neutral, weakly hydrophobic acid and hydrophilic matter by DAX-8 and XAD-4 resins (Fan *et al.* 2014; Mahdavi *et al.* 2017). From previous research, the DOM in the secondary-treated MWW could also be separated and concentrated based on hydrophobicity and hydrophilicity for further insight into the effect of the DOM on corrosion of N80 carbon steel in recirculating cooling water systems.

In the present research, we collected municipal WWTP effluent and separated the organic matter in the collected effluent into four fractions: HPOA, HPOB, WHPO and HPI, by using DAX-8 and XAD-4 resins. Electrochemical tests were used to investigate the corrosion of N80 carbon steel in different organic matter water samples and relevant control samples.

MATERIALS AND METHODS

Preparation of water samples

The secondary-treated MWW effluent was collected from Xiaoshangzhuang Municipal WWTP located in Xinxiang,

China (N35°20′33″, E113°55′33″). In the plant, a process of Aerobic(A)-Aerobic(B)-Sedimentation–Sand-Filtration–Disinfection was used to treat the MWW collected from surrounding areas. The effluent could meet the limits of discharge standard (1 Grade A) of pollutants from municipal WWTP (GB18918-2002). The effluent was treated by ultrafiltration firstly to remove particles and colloids. Then, DAX-8 resin and XAD-4 resin (both purchased from Sigma-Aldrich) were used to separate the DOM into four fractions: HPOA, HPOB, WHPO and HPI. The detail of the process and the results are shown in Figure 1 and Table 1.

As shown in Figure 1, the collected MWW effluent firstly flows through an ultrafiltration system (Guangzhou Chaoyu Membrane Ltd Co.) with a 10 kilodalton molecular weight cutoff, to remove the particles and colloid particles. Secondly, the water flows through a DAX-8 resin bed and then flows through a XAD-4 resin bed after adjusting the pH to 2. Thirdly, 0.1 mol/L HCl solution and 0.1 mol/L NaOH solution are used to wash the DAX-8 resin bed and the XAD-4 resin bed to obtain HPOA, HPOB, WHPO and HPI. The pH of the four samples is adjusted to around 7 before further electrochemical tests. Lastly, we use activated carbon to treat part of the water samples and adjust slightly the pH and conductivity to obtain control samples for the four organic fraction water samples. The characteristics of the water samples are shown in Table 1. The absorbance at 254 nm (UV254) was the main parameter concerned, which could reflect the concentration of the organic matter in the water samples (Zularisam *et al.* 2007; Pernet-Coudrier *et al.* 2008).

Preparation of electrodes

All the electrochemical tests were carried out with a CS310 electrochemical test system (Wuhan Corrtest Instruments Corp., Ltd, China). A three-electrode arrangement was employed with the N80 carbon steel (element composition wt%: C 0.22, Si 0.22, Mn 1.35, P 0.017, S 0.011, Ni 0.02, Mo 0.01, Cr 0.05 and the rest Fe) as the working electrode (WE), the KCl-saturated calomel electrode (SCE) as the reference electrode (RE) and the platinum electrode as the counter electrode (CE). 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 polished by using emery paper to a 1,200 grit surface finish. The polished
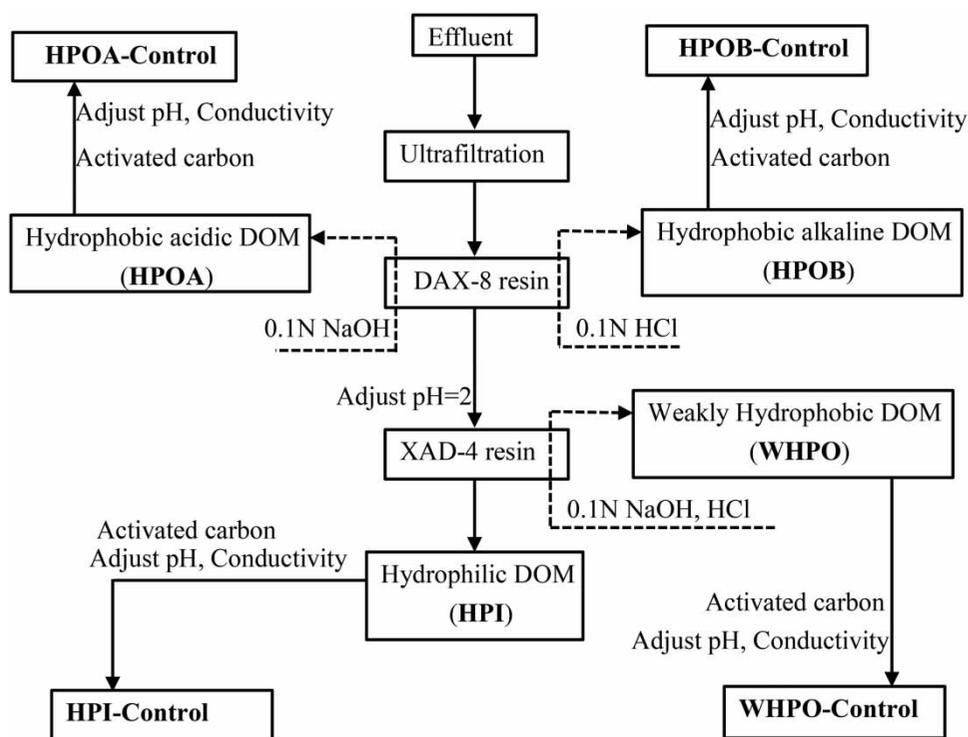
Figure 1 | Flow diagram of test solution preparation.

Table 1 | Characteristics of the water samples

Samples	UV254	Conductivity (mS/cm)	pH	DO (mg/L)
MWW effluent	0.117	2.06	7.59	4.60
After ultrafiltration	0.103	2.04	7.65	4.65
HPOA	0.115	9.42	7.09	4.23
HPOA-Control	0	9.45	7.12	4.27
HPOB	0.031	10.08	7.02	5.49
HPOB-Control	0	10.03	7.03	5.57
WHPO	0.038	5.88	6.97	5.73
WHPO-Control	0	5.94	6.96	5.77
HPI	0.011	4.24	7.13	5.76
HPI-Control	0	4.27	7.12	5.82

specimens were washed with distillate water, acetone, and distillate water, respectively.

Electrochemical tests

Electrochemical characterizations were employed to investigate the corrosion behavior of N80 carbon steel in test solutions. The three-electrode cell was kept at 25 °C (±0.5 °C) in a water bath. The open circuit potential, potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests were carried out by using a CS310 electrochemical test system (Wuhan Corrtest Instruments Corp., Ltd, China). Prior to tests, a stabilization time of 60 min was applied to obtain a stable open circuit potential. The EIS experiments were conducted in the frequency range of 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 mV to 10 mV with respect to the stable open circuit potential at a scan rate of 0.5 mV/s. We calculated the corrosion rate and parameters based on the PDP test results through corrview software supported by Wuhan Corrtest Instruments Corp., Ltd. We used Zview software to fit the EIS test data. Firstly, we chose an electrical equivalent circuit and set the initial parameters for every circuit component. Then we set the scope of the EIS data for fitting. Lastly, the fitting results and all the parameters were obtained. The fitting process was carried out by a computer. The fitting results were compared with the EIS test data to analyze the significance of the fitting method.

RESULTS AND DISCUSSION

Potentiodynamic polarization curve

The PDP curve and the R_p fitting results were used to discuss the effect of DOM in secondary-treated MWW on the corrosion of N80 carbon steel. The results are shown in Figure 2 and Table 2. UV254 was 0.115, 0.031, 0.038 and 0.011 respectively for HPOA, HPOB, WHPO and HPI. As seen in Figure 2, the presence of organic matter could affect the corrosion potential (E_o), especially for HPOA. On the whole, the corrosion rate in the presence of the four fractions was lower than that in the absence of organic matter, to some extent. As shown in Table 2, the polarization resistance (R_p) of samples was higher than that of control samples. For the four organic fraction samples, the R_p was 3,705.9 $\Omega \cdot cm^2$, 1,755.5 $\Omega \cdot cm^2$, 1,682.5 $\Omega \cdot cm^2$ and 1,622 $\Omega \cdot cm^2$, respectively. For the four control samples,

the R_p was 2,169.8 $\Omega \cdot cm^2$, 1,356 $\Omega \cdot cm^2$, 1,376.6 $\Omega \cdot cm^2$ and 1,564.1 $\Omega \cdot cm^2$, respectively. The DOM fraction could increase the R_p of the electrochemical system, decrease the corrosion current density and then decrease the corrosion rate of N80 carbon steel. Among the four kinds of organic matter, HPOA showed the highest effect on the corrosion of N80 carbon steel. In the presence of HPOA, the corrosion rate of N80 carbon steel was 0.08227 mm/a. In contrast, in the absence of HPOA, the corrosion rate of N80 carbon steel was 0.14051 mm/a. HPI showed just a little inhibition effect on the corrosion of N80 steel. The corrosion rate in the presence of HPI was 0.18796 mm/a, and the corrosion rate of the control sample was 0.19493 mm/a. That may be due to the low concentration of HPI (UV254 is 0.011, as seen in Table 1) in the water sample. The inhibition effect of HPOB and WHPO on the corrosion of N80 carbon steel was also visible. The corrosion rate was 0.17367 mm/a and 0.18121 mm/a in the presence of HPOB
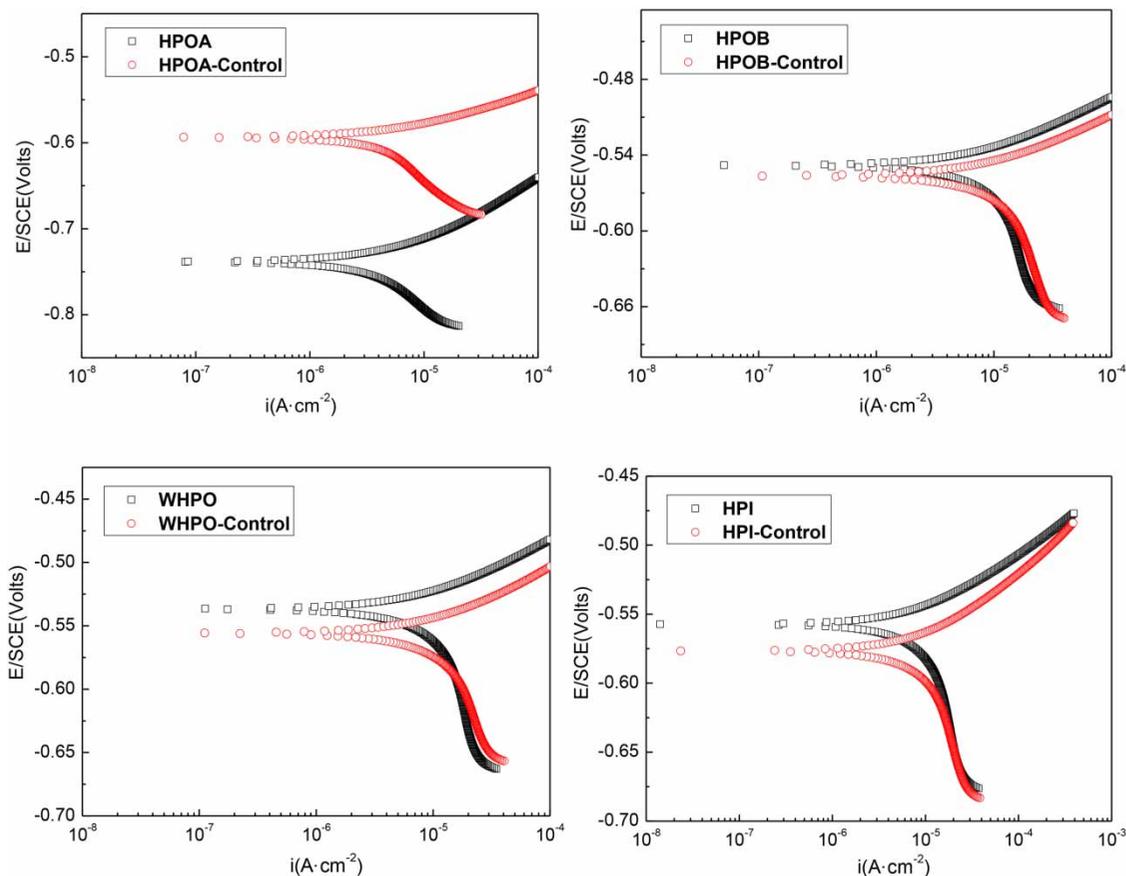

Figure 2 | PDP curves of N80 carbon steel in different water samples.

Table 2 | The R_p fitting results of the PDP curves

Samples	Corrosion rate (mm/a)	R_p ($\Omega \cdot cm^2$)	$I_o \times 10^{-5}$ (A/cm²)	E_o (V)
HPOA	0.08227	3,705.9	0.70393	−0.73994
HPOA-Control	0.14051	2,169.8	1.2023	−0.59675
HPOB	0.17367	1,755.5	1.486	−0.55016
HPOB-Control	0.22484	1,356	1.9238	−0.55852
WHPO	0.18121	1,682.5	1.5505	−0.53875
WHPO-Control	0.22147	1,376.6	1.895	−0.55771
HPI	0.18796	1,622	1.6083	−0.55951
HPI-Control	0.19493	1,564.1	1.6679	−0.57847

Where: E_0 is open circuit potential, I_0 is the corrosion current density under open circuit conditions and R_p is polarization resistance.

and WHPO, respectively. The corrosion rate of the corresponding control samples was 0.22484 mm/a and 0.22147 mm/a. In contrast with the control samples, the corrosion rate of N80 carbon steel decreased 41%, 23%, 18% and 4% in the presence of HPOA, HPOB, WHPO and HPI, respectively.

The PDP curve and the R_p fitting results were further confirmed by the EIS test results.

Electrochemical impedance spectroscopy

We investigated the EIS of the N80 carbon steel in the water samples and control samples. According to the Zview software (Wuhan Corrtest Instruments Corp., Ltd, China), an electrical equivalent circuit (Figure 3) was used to fit the EIS test results.

According to the electrical equivalent circuit, Equations (1)–(5) show the relationship between the electrochemical impedance (Z) and the parameters (R_s, C_t, C, R_t, C_1, T_1, P_1, R_1, C_2, T_2, P_2, R_2, C_{dl}, T_{dl} and P_{dl}), where R_s is the solution resistance; ω is the angular frequency; j is $\sqrt{-1}$;
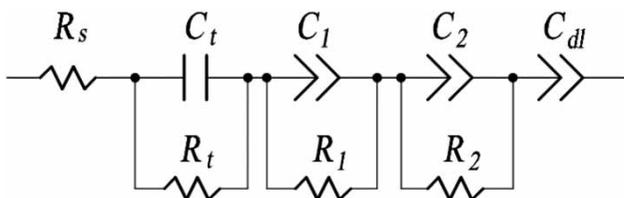
Figure 3 | Electrical equivalent circuit for fitting the EIS test results.

C_t is the solution capacitance (the capacitance between anode and cathode); R_t is the charge transfer resistance; C_1 is the film capacitance of the anode; R_1 is the film resistance of the anode; C_2 is the film capacitance of the cathode; R_2 is the film resistance of the cathode; C_{dl} is the double layer capacitance (Zhang 2010). The fitting parameters are shown in Table 3.

$$Z = R_S + \frac{1}{\frac{1}{C_t} + \frac{1}{R_t}} + \frac{1}{\frac{1}{C_1} + \frac{1}{R_1}} + \frac{1}{\frac{1}{C_2} + \frac{1}{R_2}} + C_{dl} \quad (1)$$

$$C_t = \frac{1}{j\omega C} \quad (2)$$

$$C_1 = \frac{1}{T_1 \times (j\omega)^{P_1}} \quad (3)$$

$$C_2 = \frac{1}{T_2 \times (j\omega)^{P_2}} \quad (4)$$

$$C_{dl} = \frac{1}{T_{dl} \times (j\omega)^{P_{dl}}} \quad (5)$$

where C is the capacitance between work electrode and counter electrode, and P_i ($i = 1, 2, dl$) and T_i ($i = 1, 2, dl$) are the parameters for calculating C_1, C_2 and C_{dl}.

As seen in Figure 4, the fitting results are in good agreement with the EIS test results. In other words, the chi-squared values as shown in Table 3 are much less than 0.01, which further confirms that the electrical equivalent circuit and the fitting equations are credible.

For the four Nyquist plots, the radius of the semicircle for samples in the Nyquist plots is larger than for the control samples, especially for HPOA. It indicates that the electrochemical impedance of the organic samples is larger than that of the control samples. This difference of organic matter resulted in the difference of the Nyquist plots. Otherwise, HPOA showed much more effect on the Nyquist plot than the other three fractions. Another reason could be found from the concentration of DOM in the samples. The UV254 of the four samples was 0.115, 0.031, 0.038 and 0.011 (Table 1), respectively, which reflected the concentration of DOM in the samples. Higher concentration of DOM may be the

Table 3 | The fitting parameters of EIS tests of N80 carbon steel

	R_s	$C \times 10^{-7}$	R_t	$T_1 \times 10^{-4}$	P_1	R_1	$T_2 \times 10^{-4}$	P_2	R_2	T_{dl}	P_{dl}	Chi-squared
HPOA	12.21	2.2791	8.6	6.4884	0.98522	1291	3.4958	0.74492	938.8	0.5515	2.39	0.0002554
HPOA-Control	11.22	3.0311	9.414	7.4043	0.87167	750.8	32.253	0.56915	148.9	0.12467	2.112	0.0015353
HPOB	12.09	2.6245	5.589	5.5426	0.87517	697.2	9.7391	0.62444	335.2	0.06182	2.083	0.0031523
HPOB-Control	11.44	1.8879	7.3	4.4723	0.8349	623.3	20.473	0.56573	132.6	0.09298	2.075	0.0013609
WHPO	18.23	3.0018	14.02	1.5667	0.81987	1,064	0.011755	0.39111	1256	0.20879	2.406	0.000346
WHPO-Control	25.93	31.291	3.588	0.82924	0.85865	439.3	0.0011172	0.62856	276.9	0.19333	2.093	0.0021087
HPI	20.64	1.879	16.26	9.6389	0.82662	913.8	0.0023339	0.50083	50.79	0.12657	2.269	0.0004003
HPI-Control	23.67	4.9981	18.77	11.213	0.85027	670.4	0.0058054	0.46818	134.8	0.21357	2.285	0.0004672
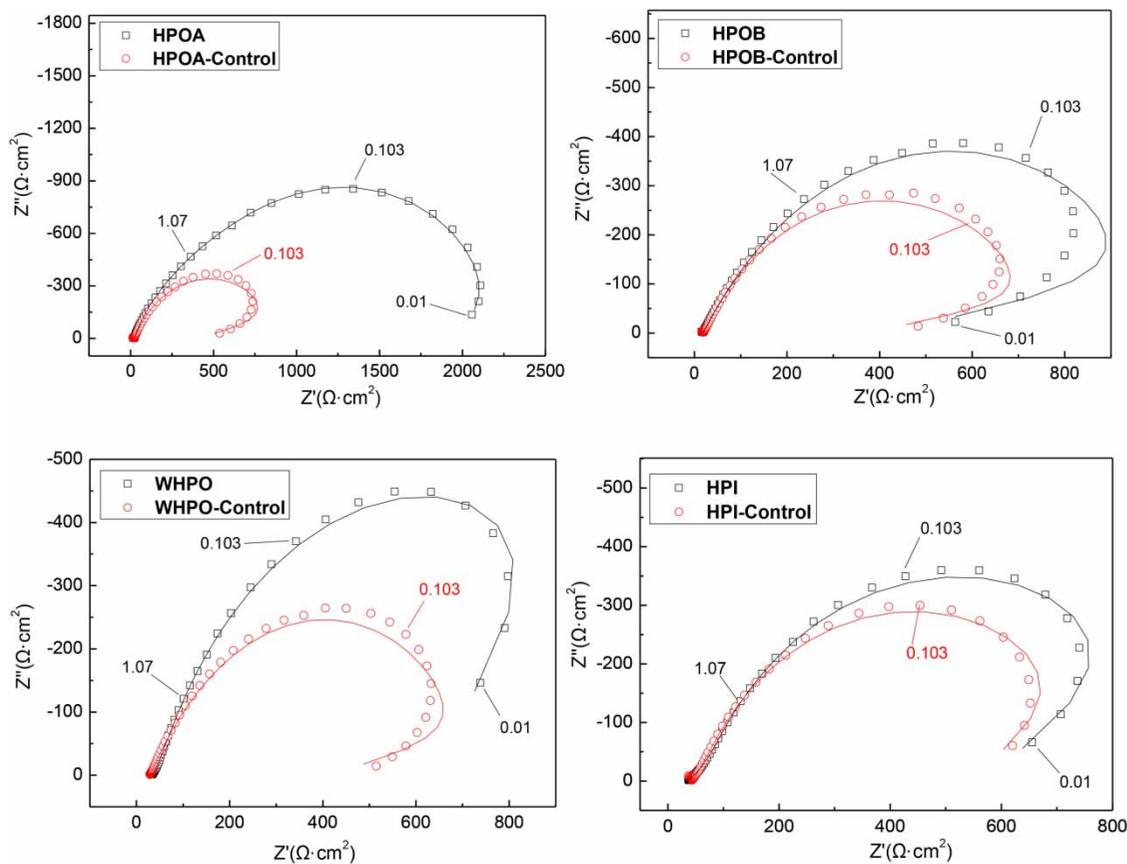
Figure 4 | Nyquist plots of N80 carbon steel (Z′ is the real part of the electrochemical impedance; Z′′ is the imaginary part of the electrochemical impedance).

dominant reason that the radius of the semicircle in the Nyquist plots is larger than for the other three samples. The results were in accordance with the PDP results.

As shown in Table 1, the main difference between sample and control sample is the UV254 data, which reflect the concentration of DOM. Organic matter in the water sample could adsorb onto the N80 carbon steel electrode (WE) and platinum electrode (CE), to form a protective film, which could inhibit the electron transfer. As shown in Figure 3, we use a multiple circuit of capacitance and resistance to fit the electrochemical impedance

of the protective film of organic matter on the electrode. Table 3 shows the fitting parameters of EIS of N80 carbon steel in the water samples and control samples. According to the conductivity of the water samples (Table 1), the solution resistance (R_s) of sample 1 was similar to that of sample 2, while the R_s of sample 3 was similar to that of sample 4. The R_s could reflect the conductivity of the water samples.

CONCLUSIONS

Four dissolved organic fractions (hydrophobic acidic, hydrophobic alkaline, weakly hydrophobic and hydrophilic) were isolated from municipal wastewater plant effluent by using DAX-8/XAD-4 resin adsorption techniques. The UV254 absorbent of the water samples containing the four fractions was 0.115, 0.031, 0.038 and 0.011, respectively. We used electrochemical methods (PDP and EIS) to investigate corrosion characteristics of N80 carbon steel in the different water samples and relevant control samples. In contrast with the control samples, the corrosion rate of N80 carbon steel in the four DOM water samples decreased 41%, 23%, 18% and 4%, respectively for hydrophobic acidic, hydrophobic alkaline, weakly hydrophobic and hydrophilic. Electrical equivalent circuit and fitting equations were used to fit the test results and a very high fitting degree was visible. The EIS results further conformed the PDP results, and revealed the action mechanism of organic matter on N80 carbon steel. Organic matter could adsorb onto the surface of the N80 carbon steel and the counter electrode to form a protective film. And then the corrosion rate of the N80 carbon steel decreased.

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