

# Inhibition mechanism of nitrite on the corrosion of carbon steel in simulated cooling water systems

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The corrosion inhibition mechanism of sodium nitrite on carbon steel has been carefully studied in different simulated cooling water solutions by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The obtained results showed that the corrosion inhibition increases by increasing the nitrite concentration up to 9 mM in 5 mM chloride solution at 25 °C. The corrosion state and corrosion current density are strongly depended upon the nitrite and chloride concentration, solution temperature, and applied potential. The interaction of nitrite with metal surface follows the Langmuir adsorption isotherm and the adsorption is as a physisorption process in a neutral solution.

## KEYWORDS

carbon steel, cooling water, EIS, nitrite, polarization

## 1 | INTRODUCTION

Inorganic inhibitors have been widely used to reduce the effects of corrosion on metallic-industrial equipment in different corrosive environments.<sup>[1–3]</sup> Nitrite as an inorganic inhibitor has attracted a great deal of attention in the literature due to its low cost and relatively good inhibition performance.<sup>[4–6]</sup> Also, nitrite has been utilized in a synergistic function with other inhibitors, e.g., with molybdate<sup>[7]</sup> to provide the oxidizing feature when there is a lack of sufficient oxygen within the solution.<sup>[8,9]</sup> Nevertheless, the main risk of nitrite is related to the reduction in its concentration to less than what is required for an effective inhibition leading to pitting corrosion.<sup>[10,11]</sup>

The inhibition mechanism of nitrite has been studied by many researchers.<sup>[12–14]</sup> In the case of iron, it has been proposed that the nitrite ions act as an oxidizing agent and they promote conversion of ferrous to ferric resulting in the formation of a robust and stable passive film of iron oxides on the metal surface.<sup>[15–18]</sup> The passive film mainly consists of magnetite and maghemite as inner and outer parts, respectively.<sup>[4,19,20]</sup>

The influence of nitrite inhibition on the corrosion of iron has been studied under different corrosion conditions such as solution temperature,<sup>[5,21–23]</sup> concentration of nitrite,<sup>[17,23,24]</sup> concentration of aggressive ions,<sup>[21,25]</sup> solution pH.<sup>[26,27]</sup> In this regard, the main attention has been concentrated on the control of nitrite concentration in an adequate region to attain the best inhibitive properties and thus reduce the risk of pitting corrosion.<sup>[28]</sup> Some research have been devoted to the evaluation of the protective function of nitrite ions on the steel used for concrete applications by means of a simulated environment<sup>[24,29,30]</sup>, where often a high concentration of nitrite has been utilized to enhance the system robustness.<sup>[27]</sup>

It has been reported that the nitrite concentration strongly depends on the pH range and the chloride contamination of the solution that was utilized in the operational conditions. Negative effect may be attained by addition of excessive amounts of nitrite at low pH values because of the great influence of hydroxyl groups in the inhibition mechanism of nitrite.<sup>[13,26]</sup> Mohana and Badiea<sup>[22]</sup> studied the inhibition feature of nitrite-borax system on carbon steel in various conditions and they found the active state in presence of

**TABLE 1** Chemical composition of carbon steel

Element	C	Mn	P	S	Si	Cr	Cu	Mo	Ni	V	Fe
Composition (wt%)	0.35	1.06	0.04	0.04	0.10	0.40	0.40	0.15	0.40	0.08	Balance

nitrite. Hayyan et al.<sup>[17]</sup> showed that the inhibition efficiency of nitrite decreases with increasing the concentration of chloride ions in a neutral solution under dynamic conditions.

Recently, Lee et al.<sup>[31]</sup> investigated the effect of nitrite concentration on the corrosion behavior of carbon steel in tap water. They reported that the corrosion rate decreases significantly when the nitrite concentration becomes greater than a critical value at which a transition from active to passive state is observed by the polarization curves. Although some studies have reported about the nitrite inhibition, the inhibition mechanism of nitrite in a neutral solution at low chloride concentration and at various temperatures that is mainly encountered in cooling water systems has not been investigated.

The aim of this work is to study the inhibition mechanism of nitrite in simulated cooling water solutions at neutral region. To do this efficiently, the effect of different concentrations of chloride and nitrite and at different temperatures have been studied by using the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

## 2 | EXPERIMENTAL

### 2.1 | Materials and solutions

Both sodium nitrite as an inhibitor and sodium chloride as a corrosive agent were purchased from Merck. Double distilled water was used for all of the experiments. The chemical composition of carbon steel (working electrode) is given in Table 1. The metallic specimens were mounted using epoxy resin and isolating an area for the electrochemical experiments (a square surface with dimensions of  $1 \times 1 \text{ cm}^2$ ). The surface of the steel was consecutively abraded with 60, 120, 320, 600, 800, 1200, and 2000 grades of emery papers. Then, it was rinsed twice with water, acetone and finally with distilled water and then immediately dried with warm air to avoid any corrosion initiation.

Various aqueous solutions were prepared to study the influence of nitrite concentration, solution temperature, and

chloride concentration on the corrosion behavior of carbon steel samples in a systematic way. As the first step, the concentration of nitrite was varied from 0 to 17 mM when the chloride concentration and solution temperature were kept constant at the values of 5 mM and 25 °C, respectively. In the next step, the effect of solution temperature was inspected at 25, 45, and 65 °C in the solution with an optimum concentration of nitrite, resulting in maximum inhibition efficiency. Finally, the concentration of chloride ions was changed from 0 to 10 mM at the optimum nitrite concentration and at 25 °C. For all experiments, the temperature was thermostatically controlled using a water bath with an accuracy of  $\pm 0.1$  °C.

It is expected that the pH may also vary with the incorporation of nitrite ions.<sup>[27]</sup> The effect of nitrite concentration on the pH is given in Table 2. As it can be seen, the pH values are slightly decreased by increasing the nitrite concentration because of  $\text{OH}^-$  consumption. This observation is in good agreement with experiments of Garces et al.<sup>[26,27]</sup>

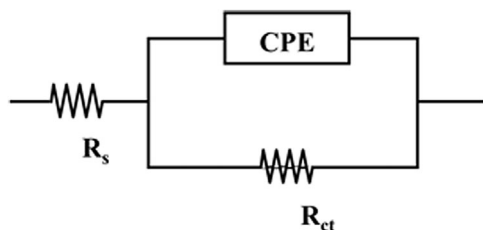
### 2.2 | Electrochemical measurements

Electrochemical measurements were carried out using an Autolab potentiostat/galvanostat (PGSTAT 302N) in a three-electrode glass cell containing 100 ml of solution. In this setup, a graphite rod was used as the counter electrode, a saturated calomel electrode (SCE) was used as the reference electrode and the carbon steel samples were used as the working electrode. During the time of measurement, especial care was taken for the specimen to be fully immersed in the solution and not touch the side walls or the bottom of the glass cell. In addition, all electrochemical measurements were repeated at least two times until a good reproducibility was observed and the average data have been reported.

For the potentiodynamic polarization test, the potential sweep was started from  $-0.4 \text{ V}$  to about  $0.5 \text{ V}$  relative to the OCP value at a scan rate of  $1 \text{ mV s}^{-1}$ . In order to quantitatively inspection of potentiodynamic polarization data, Tafel analysis was done to calculate the anodic ( $\beta_a$ ) and

**TABLE 2** Variation of initial solution pH with nitrite concentration

Nitrite concentration (mM)	0	1	3	7	9	17
pH	7.05	6.98	6.94	6.89	6.85	6.78



**FIGURE 1** Equivalent circuit used to fit the impedance data for carbon steel

cathodic ( $\beta_c$ ) slopes by extrapolation of the relevant branches at least  $\pm 100$  mV away from  $E_{\text{corr}}$  value where a linear behavior was observed for one decade. In this way, the corrosion current ( $i_{\text{corr}}$ ) was determined from the intersection of the extrapolated anodic and cathodic lines.

The EIS spectra were recorded at an amplitude perturbation of 10 mV versus OCP over the frequency range of 100 kHz to 10 mHz. The obtained impedance spectra were fitted to the equivalent circuit known as Randles illustrated in Figure 1 by means of Zview software.

### 3 | RESULTS AND DISCUSSION

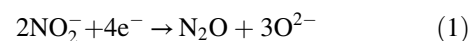
#### 3.1 | Open circuit potential measurement

The change in the values of open circuit potential (OCP) for 5 mM chloride solution with different nitrite concentrations at 25 °C is depicted in Figure 2. Based on these results, it is apparent that a steady state condition is achieved after 50 min immersion and it does not change during the electrochemical measurements for at least 40 min (see Figure 2). This procedure was also applied for the other effective parameters and a similar behavior was observed.

#### 3.2 | Effect of nitrite concentration

Figure 3 shows the potentiodynamic polarization curves of carbon steel in 5 mM chloride solution with different

concentrations of nitrite ions at 25 °C. It appears that carbon steel is in active state of corrosion in all nitrite concentrations. However, the data suggest that the system has a tendency for passivation at high applied potentials when the nitrite concentration is greater than 9 mM. Similar corrosion behavior of carbon steel in a neutral solution and the presence of nitrite ions has been reported before.<sup>[31]</sup> To interpret this behavior, it is useful to describe the inhibition mechanism of nitrite ion. It progresses through the adsorption of nitrite on the metal surface<sup>[32]</sup> and then it undergoes a reduction reaction leading to the generation of oxygen ions as follows<sup>[17,31]</sup>:

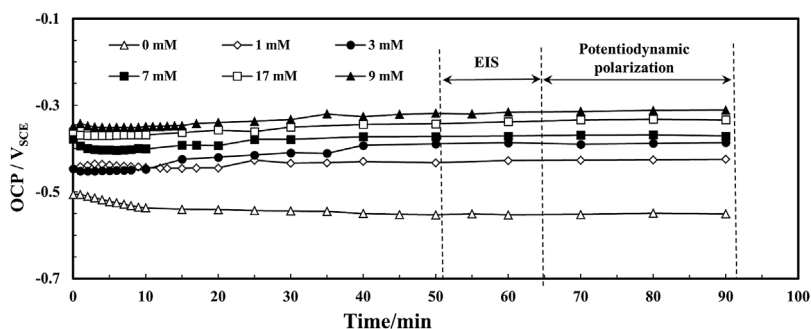


In fact, reduction of nitrite ions results in the generation of oxygen in the form of  $\text{O}^{2-}$  ions which stimulate the oxidization of ferrous ions to ferric.<sup>[9]</sup> In an alkaline solution, it results in the formation of the stable passive film of maghemite on the metal surface which can be summarized as the following reaction<sup>[16,30,31]</sup>:

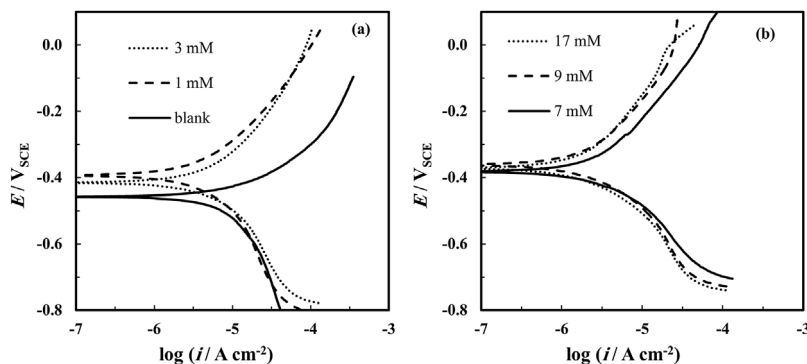


According to this equation, it is clear that hydroxyl groups as well as nitrite ions have a vital role in the passivation of iron.<sup>[28]</sup> Therefore, the active dissolution of carbon steel in Figure 3 can be related to two main reasons: (a) the lack of hydroxyl groups in the neutral solution and (b) the high concentration of chloride ions as the corrosive ions preventing the growth of a passive film<sup>[3,13,27]</sup> which will be discussed in more detail later.

The polarization parameters reflecting the inhibition effect of nitrite are presented in Table 3. Addition of nitrite to the solution up to 9 mM produces a shift of corrosion potential,  $E_{\text{corr}}$  toward more positive values and decreases significantly corrosion current density. These observations confirm the anodic inhibition mechanism of nitrite ions which has been previously reported.<sup>[8,23,28]</sup>



**FIGURE 2** Variation of open circuit potential (OCP) with time for corrosion of carbon steel in 5 mM chloride solution containing different concentrations of nitrite at 25 °C



**FIGURE 3** Potentiodynamic polarization curves of carbon steel in a 5 mM chloride solution with (a) 0, 1, and 3 mM and (b) 7, 9, and 17 mM of nitrite at 25 °C. Scan rate: 1 mV s<sup>-1</sup>

The values of  $\beta_c$  decrease continuously with increasing the concentration of nitrite ions which indicates that the cathodic reaction is accelerated by shifting from oxygen reduction to that of nitrite reduction according to Eq. (1).<sup>[3,23]</sup> This can facilitate the nitrite inhibition process on the iron surface.<sup>[17]</sup>

On the other hand, the increase of nitrite dosage causes two changes in the anodic part of the potentiodynamic polarization curves. First, the values of the anodic slopes ( $\beta_a$ ) are increased (Table 3). Second, the anodic branches are displaced toward the left hand side of the polarization plot (see Figure 3) indicating a reduction of current density.<sup>[33]</sup> Based on these evidences, it is expected that an oxide layer will form on the carbon steel surface upon increasing the nitrite concentration. Since this oxide layer is unable to provide for complete passivation, it is likely the formation of Fe(II) oxide/hydroxide mainly in the form of magnetite which will result in a lower protection compared to that of maghemite as described previously.<sup>[17,34]</sup>

Table 3 shows that  $i_{\text{corr}}$  increases slightly and  $E_{\text{corr}}$  shifts negatively with further addition of 17 mM of nitrite ions because of competitive adsorption between nitrite ions and hydroxyl groups on the iron oxide/hydroxide film where the excessive adsorption of nitrite ions in the absence of sufficient hydroxyl groups (in a neutral solution) is not

efficient to passivate the iron surface according to Eq. (2). This can be related to the oxidizing nature of nitrite which accelerates the anodic dissolution of iron ions.<sup>[26]</sup> This observation on the corrosion of carbon steel was reported by Mohana and Badia<sup>[22]</sup> for nitrite and Meziane et al.<sup>[35]</sup> for molybdate ions.

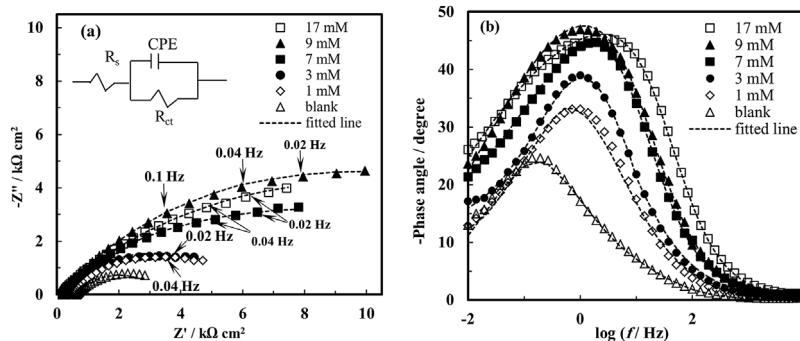
It is noteworthy that as an electroactive species, nitrite can undergo both reduction and oxidation reactions.<sup>[12,29]</sup> However, in the case of corrosion inhibition, many researchers have explained the oxidizing effect of nitrite ions via Eq. (4).<sup>[1,9,16]</sup> Although, it has been suggested that nitrite can be regenerated by the oxidation of ammonium ions in an aerated solution.<sup>[17]</sup>

EIS is a nondestructive test on the metal surface and it has been widely used for inspection of interfacial phenomena.<sup>[36,37]</sup> For carbon steel in a 5 mM chloride solution containing different nitrite concentrations, the EIS curves in the form of Bode phase and Nyquist diagrams are shown in Figure 4.

The presence of a single capacitive loop in the Nyquist diagrams suggests the use of an equivalent circuit with a single electrical circle known as Randles (see Figure 1). In this model,  $R_s$  is the solution resistance,  $R_{ct}$  is the charge transfer resistance and a constant phase element (CPE) is used instead of a capacitor element. Both of the  $R_{ct}$  and CPE

**TABLE 3** Polarization parameters as a function of nitrite concentration for carbon steel in a 5 mM chloride solution at 25 °C

Nitrite concentration (mM)	$E_{\text{corr}}$ (mV <sub>SCE</sub> )	$\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
Blank	-552	478	220	15.6
1	-417	442	260	6.3
3	-397	331	272	5.2
7	-381	227	287	3.1
9	-359	218	295	1.6
17	-370	196	310	2.0



**FIGURE 4** Impedance spectra recorded on the carbon steel in a 5 mM chloride solution with different concentrations of nitrite at 25 °C in the form of (a) Nyquist and (b) Bode phase diagrams

elements are related to the characteristics of the metal/solution interface.

Figure 4 shows a depressed semicircular form in the Nyquist diagrams which is caused by the dispersion of impedance data at the low frequency region as a result of the nonhomogeneity of the metal surface.<sup>[38,39]</sup> In order to provide a good fit to the impedance data, it is often necessary to substitute the CPE for the capacitance element. The impedance relation of a CPE is expressed as follows<sup>[39,40]</sup>:

$$Z_{\text{CPE}} = (Y(\omega j)^n)^{-1} \quad (3)$$

where  $Y$  and  $\omega$  are the admittance coefficient ( $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ ) and angular frequency (rad/s), respectively;  $j$  defines the imaginary number ( $\sqrt{-1}$ ) and  $n$  is the CPE exponent ( $0 \leq n \leq 1$ ). Using these parameters the ideal capacitance value of ( $C$ ) was calculated by using the following equation:

$$C = (Y/R_{\text{ct}}^{n-1})^{1/n} \quad (4)$$

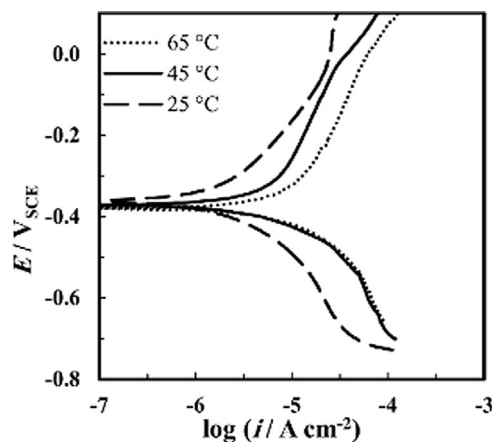
**TABLE 4** Impedance parameters for corrosion of carbon steel in a 5 mM chloride solution containing different concentrations of nitrite at 25 °C

Sodium nitrite concentration (mM)	CPE			
	$R_{\text{ct}}$ ( $\text{k}\Omega \text{ cm}^2$ )	$Y \times 10^4$ ( $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ )	$n$	$C \times 10^4$ ( $\text{F cm}^{-2}$ )
Blank	2.60	7.6	0.62	12.0
1	5.28	2.7	0.61	3.4
3	5.33	3.4	0.65	4.7
7	8.54	2.9	0.64	4.8
9	16.20	2.0	0.65	3.8
17	12.36	2.3	0.64	4.1

The validity of the EIS data was checked by using Kramers–Kronig transform at the applied frequency range and the reliability of the EIS data with respect to the stability and causality was found. All of the EIS spectra were well fitted to the Randles equivalent circuit using the Zview software and the calculated parameters are presented in Table 4.

The value of  $R_{\text{ct}}$  increases continuously and  $C$  decreases when the amount of nitrite ion varies from 0 to 9 mM indicating an increase in the resistance against development of corrosion. By further addition of nitrite to the solution and increasing the concentration up to 17 mM,  $R_{\text{ct}}$  decreases and  $C$  increases due to the negative effect of the excessive amounts of nitrite on the corrosion process. These are in very good agreement with those obtained for corrosion current density,  $i_{\text{corr}}$  by applying the polarization method and that previously reported in the literature.<sup>[26,31]</sup>

The value of  $C$  is the one that is most related to the characteristics of the interfacial layer including thickness ( $d$ ), surface area ( $A$ ), and dielectric constant ( $\epsilon$ ) that are related to



**FIGURE 5** Potentiodynamic polarization curves of carbon steel in a solution with 9 mM nitrite and 5 mM chloride and at different temperatures. Scan rate:  $1 \text{ mV s}^{-1}$

**TABLE 5** Polarization parameters as a function of temperature for carbon steel in a solution containing 9 mM nitrite and 5 mM chloride

Temperature (°C)	$E_{\text{corr}}$ (mV <sub>SCE</sub> )	$\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )
25	-359	218	295	1.6
45	-364	222	493	6.6
65	-380	254	561	12.7

each other by the following relation<sup>[36]</sup>:

$$C = \epsilon \epsilon_0 A / d \quad (5)$$

where  $\epsilon_0$  is the permittivity of free space that is equal to  $8.85 \times 10^{-12} \text{ F m}^{-1}$  and  $A$  is area of the working electrode ( $1 \text{ cm}^2$ ).

Table 4 shows a high value of capacitance ( $1200 \mu\text{F cm}^{-2}$ ) for carbon steel in the solution free of nitrite suggesting the low corrosion resistance of the steel surface against the chloride attack in the absence of nitrite. Note that the value of  $C$  decreases sharply in the presence of nitrite which indicates the great influence of nitrite inhibition. However, the calculated values of capacitance are in the range of  $340\text{--}480 \mu\text{F cm}^{-2}$  which is greater than what would be expected for a double layer capacitance value (about  $50 \mu\text{F cm}^{-2}$ ) in the form of maghemite.<sup>[41,42]</sup> This could be related to the electrically conductive nature and polarizable state of magnetite in comparison with the maghemite.<sup>[41]</sup>

The incorporation of nitrite ions into the solution up to 9 mM results in the growth of an oxide film mainly as magnetite through a solid state mechanism and it could possibly cause a decreasing in the capacitance value at the metal surface as a result of increment of the film thickness with respect to Eq. (5). However, it appears that in solutions with higher concentrations of nitrite ( $>9 \text{ mM}$ ), a little destructive effect on the oxide film resulting in further penetration of water molecules within the oxide film and increasing the dielectric constant ( $\epsilon$ ) is more likely as reported before.<sup>[23,36,39]</sup> This may cause a slight increase of  $C$  according to Eq. (5). From Table 4, it is observed that the

values of the parameter  $n$  slightly increase with nitrite concentration which is an evidence for the formation of a more uniform layer on the iron surface.<sup>[39]</sup>

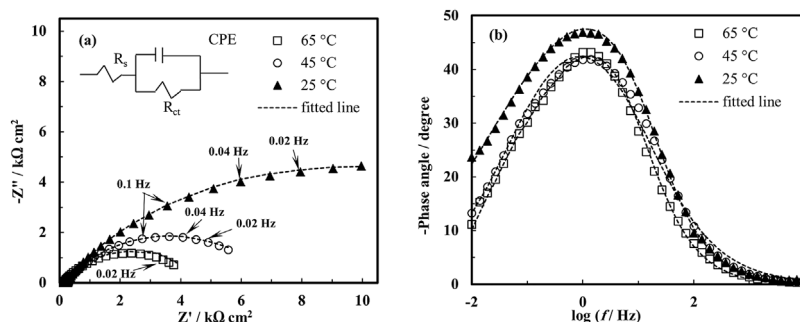
The results obtained from both EIS and polarization methods suggest that 9 mM nitrite is an optimum concentration to protect carbon steel exposed to a solution with 5 mM chloride at 25 °C. In the present work, this concentration has been chosen as a basis of nitrite content within the solution to evaluate the other effective parameters.

### 3.3 | Effect of temperature

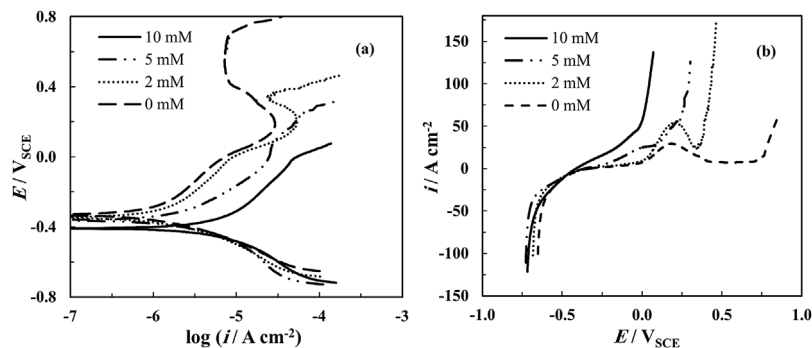
In the industrial applications, temperature is an important parameter which may change during the life time of the equipment and cause serious corrosion problems on the carbon steel surface. The polarization curves for a solution containing 5 mM chloride and 9 mM nitrite in a temperature range from 25 to 65 °C (which is often used in cooling water systems) are shown in Figure 5. The results of the Tafel analysis for the potentiodynamic polarization data are given in Table 5.

When the temperature of the solution rises, the corrosion current density,  $i_{\text{corr}}$ , increases and  $E_{\text{corr}}$  shifts to more negative values. It is clear that both  $\beta_c$  and  $\beta_a$  increase with temperature. However, the variation of  $\beta_a$  is much greater than that of  $\beta_c$ . All of these observations indicate that the increase in temperature generally facilitates metal ion dissolution by further activation of the metal surface<sup>[5,23]</sup> and also decrease in the resistance of oxide film on the metal surface.<sup>[20,21]</sup>

Figure 6 shows the EIS spectra for carbon steel and the impedance parameters are presented in Table 6. An increase



**FIGURE 6** Impedance spectra recorded on carbon steel in a solution with 9 mM nitrite and 5 mM chloride and at various temperatures in the form of (a) Nyquist and (b) Bode phase diagrams



**FIGURE 7** Potentiodynamic polarization curves in (a) logarithmic and (b) linear scale of current for carbon steel in 9 mM nitrite solutions containing different concentrations of chloride at 25 °C. Scan rate: 1 mV s<sup>-1</sup>

in temperature produces a significant decrease in the value of  $R_{ct}$  and an increase in the value of  $C$ . Both of these are clear indications of acceleration of iron dissolution similar to that observed in the polarization tests. The increase of  $C$  can be attributed to the fact that the increase of temperature causes deterioration of the oxide film formed on the steel surface and thus decrease in the film thickness according to Eq. (8). Moreover, it is found from Table 6 that the parameter  $n$  decreases with an increase in temperature indicating higher porosity and enhancement in the roughness of steel surface due to the increase in the amount of corrosion products.<sup>[36]</sup>

### 3.4 | Effect of chloride concentration

The corrosion inhibition of nitrite in cooling waters, boilers and similar equipment is sensitive to the chloride concentration which is generated from the chloride contamination of water. The potentiodynamic polarization curves (in both logarithmic and linear scale of current) for the effect of chloride ions (in the range may be encountered in cooling water) on the corrosion of carbon steel in a solution with 9 mM nitrite at 25 °C are presented in Figure 7. Active dissolution at OCP is obvious in all of the plots even for the solution free of chloride. In a neutral solution, the lower content of hydroxyl groups within the solution hinders the

formation of the robust layer oxide of maghemite on the steel surface regardless of the nitrite/chloride ratio as previously discussed.

On the other hand, there is a competition process between chloride and passivating ions to get adsorbed on the metal surface where chloride ions trigger the iron dissolution by the formation of soluble salt of iron(II) chloride while hydroxyl groups and nitrite ions facilitate the passivity of the metal surface.<sup>[28,43]</sup> However, for electrolytes with less than 5 mM chloride and at high applied potentials, a passive region is observed in the polarization curves (Figure 7a). This can be attributed to the anodic oxidation of ferrous to ferric which results in the conversion of the outer part of the oxide film from magnetite to maghemite as also studied by Daub et al.<sup>[41]</sup> In this situation, the effect of passivating ions overcomes that of the chloride resulting in the formation of a strong passive film and decrease of the corrosion current density.

The values of the parameters obtained from the polarization methods for studying the effect of chloride concentration are presented in Table 7. When the chloride concentration increases from 0 to 10 mM,  $E_{corr}$  shifts negatively and  $i_{corr}$  increases steadily due to the increase in dissolution rate of ferrous as a result of higher activation of the metal surface. In addition,  $\beta_a$  decreases slightly with the addition of chloride up to 5 mM showing the corrosive effect

**TABLE 6** Impedance parameters for corrosion of carbon steel in a solution with 9 mM nitrite and 5 mM chloride at various temperatures

Temperature (°C)	$R_{ct}$ (k $\Omega$ cm <sup>2</sup> )	CPE		
		$Y \times 10^4$ ( $\Omega^{-1}$ s <sup>n</sup> cm <sup>-2</sup> )	$n$	$C \times 10^4$ (F cm <sup>-2</sup> )
25	16.20	2.0	0.65	3.8
45	6.76	3.2	0.61	5.2
65	4.63	4.2	0.60	6.5

**TABLE 7** Electrochemical parameters calculated from potentiodynamic polarization method for corrosion of carbon steel in a 9 mM nitrite solution with various concentrations of chloride at 25 °C

Chloride concentration (mM)	$E_{corr}$ (mV <sub>SCE</sub> )	$\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	$i_{corr}$ ( $\mu$ A cm <sup>-2</sup> )
0	-333	174	433	1.1
2	-344	189	418	1.4
5	-359	218	295	1.6
10	-414	270	432	6.1

of chloride ions that stimulate the anodic dissolution.<sup>[3,44]</sup> At the same time,  $\beta_c$  increases slightly with chloride content suggesting the influence of chloride ions on the reduction of nitrite ions.

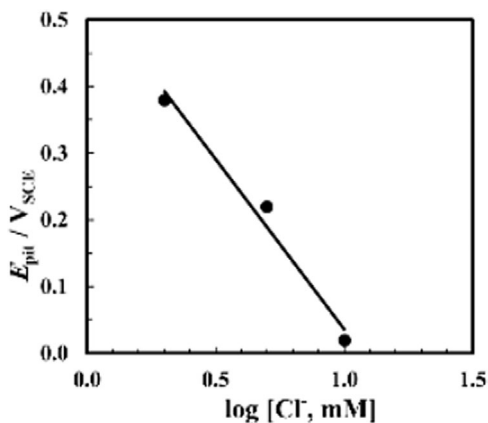
For the systems having the ability to passivate at high applied potentials, pitting corrosion may start at the pitting potential ( $E_{\text{pit}}$ ) where the corrosion current density rapidly increases (see Figure 7). This indicates the breakdown of the pseudo passive film and implies the beginning of pitting corrosion. This event is originated by the penetration of chloride ions into the passive film under high applied potentials, and it promotes localized corrosion in the active sites.<sup>[43,45]</sup>

The plot of  $i$  versus  $E$  in linear scale (Figure 7b) is used to easily determine the  $E_{\text{pit}}$  values. If the quantity of chloride ions decreases from 10 to 0 mM,  $E_{\text{pit}}$  increases considerably from 0.02 to 0.70 V suggesting the increase in the protective level of the passive film. Variations of  $E_{\text{pit}}$  with chloride concentration are shown in Figure 8 where a linear dependency is observed corresponding following logarithmic relationship<sup>[5,43]</sup>:

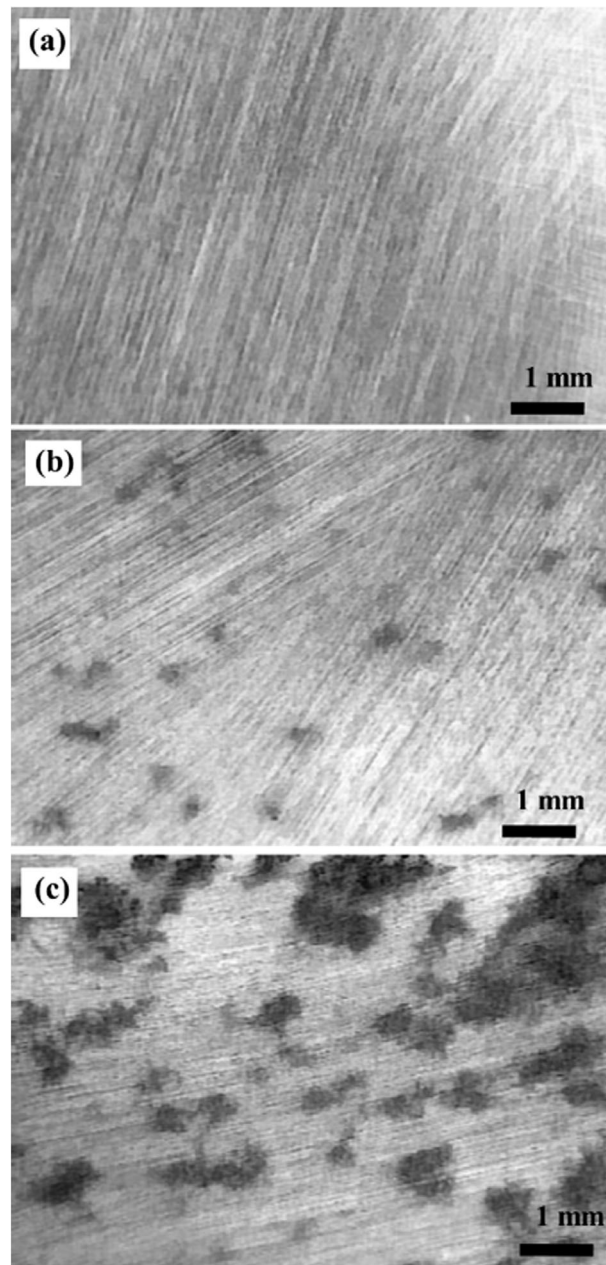
$$E_{\text{pit}} = a - b \log[\text{Cl}^-] \quad (6)$$

where  $a$  and  $b$  are constants and depend on the corrosive condition. With respect to the results presented in Figure 9, the values of  $a$  and  $b$  in a 9 mM nitrite solution at 25 °C are 0.546 and 0.509 V decade<sup>-1</sup> ( $R^2 = 0.98$ ).

Photographs of the surface of the specimens after performing potentiodynamic polarization test in a 5 mM nitrite solution at different chloride concentrations (0, 2, and 5 mM) are shown in Figure 9. It is clear that there exists no evidence of pitting on the metal surface (Figure 9a) in the absence of chloride. However, pitting corrosion takes place (Figure 9b and c) in the presence of chloride in



**FIGURE 8** Dependence of  $E_{\text{pit}}$  on the logarithm of chloride concentration for carbon steel in 9 mM nitrite solution containing different concentrations of chloride at 25 °C

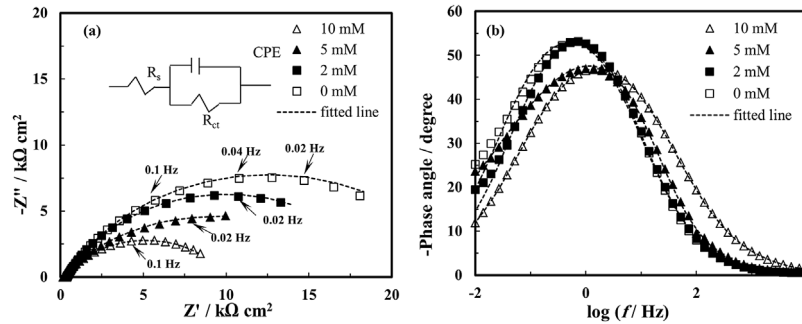


**FIGURE 9** Photographs of surface of specimen after potentiodynamic polarization test in 9 mM nitrite solution with (a) blank, (b) 2 mM, and (c) 5 mM chloride concentration at 25 °C

the solution. Note that the electrolyte with 5 mM chloride has a larger size of pits compared to the one with 2 mM chloride because of the higher degree of corrosive attack on the passive film.

Figure 10 depicts the impedance diagrams for the effect of chloride concentration on the corrosion behavior of carbon steel in a solution with 9 mM nitrite at 25 °C. It is clear that all of the Nyquist plots involve a single semicircle confirming the active state of the carbon steel observed in the potentiodynamic polarization test. The impedance parameters of the EIS spectra are provided in Table 8.





**FIGURE 10** Impedance spectra recorded on carbon steel in 9 mM nitrite solution with different concentrations of chloride at 25 °C, in the form of (a) Nyquist and (b) Bode phase diagrams

It is found that the values of  $R_{ct}$  decrease and the values of  $C$  increase continuously with an increase in the quantity of corrosive ions. This can be directly related to the attack of chloride ions over the oxide film on the metal surface.<sup>[13,44]</sup> The reduction of the parameter  $n$  with an increase in chloride concentration indicates the increase of the roughness of the solution/metal interface as a result of chloride attack preventing the formation of a uniform oxide layer.

### 3.5 | Adsorption isotherm

The nature of interaction between the nitrite and metal surface can be further investigated by using the isotherm adsorption. Among several adsorption isotherms proposed to evaluate the adsorption mechanism, Langmuir isotherm had the best fit to the experimental data according to the following equation<sup>[22]</sup>:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (7)$$

where  $C_{inh}$  is the concentration of inhibitor,  $K_{ads}$  is the adsorptive equilibrium constant, and  $\theta$  is the surface coverage degree which can be calculated by the potentiodynamic polarization results according to:

$$\theta = \frac{I_{blank} - I_{inh}}{I_{blank}} \quad (8)$$

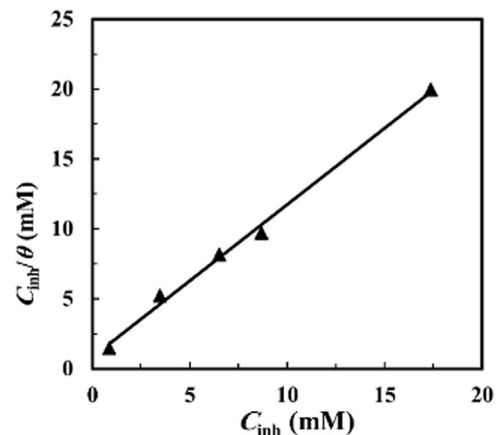
where  $I_{blank}$  and  $I_{inh}$  are the corrosion current density of uninhibited and inhibited specimens. The values of coverage degree for carbon steel in 5 mM chloride solution with different nitrite concentrations at 25 °C (see Table 3) were calculated. The linear relation of  $C_{inh}/\theta$  versus  $C_{inh}$  is depicted in Figure 11. The experimental data are well described by the Langmuir adsorption isotherm with a very good regression coefficient ( $R^2 = 0.995$ ). This recommends that the adsorbed layer on the carbon steel surface in the presence of nitrite is of monolayer in nature. Additionally, with respect to Eq. (7) the adsorptive equilibrium constant,  $K_{ads} = 915.4 \text{ M}^{-1}$  was calculated from the intercept of the plot presented in Figure 11.

The  $K_{ads}$  is related to the standard Gibbs energy of adsorption ( $\Delta G_{ads}^0$ ) by using the following equation<sup>[39]</sup>:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad (9)$$

**TABLE 8** Impedance parameters for corrosion of carbon steel in a 9 mM nitrite solution with various concentrations of chloride at 25 °C

Chloride concentration (mM)	$R_{ct}$ ( $\text{k}\Omega \text{ cm}^2$ )	CPE		
		$Y \times 10^4$ ( $\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ )	$n$	$C \times 10^4$ ( $\text{F cm}^{-2}$ )
0	23.65	1.4	0.75	2.1
2	20.02	1.5	0.70	2.4
5	16.20	2.0	0.65	3.8
10	10.01	2.3	0.59	4.1



**FIGURE 11** Langmuir adsorption plot for carbon steel in 5 mM chloride solution at 25 °C

where  $R$  is the universal gas constant and  $T$  is the absolute temperature. By application of Eq. (9), value of  $\Delta G_{\text{ads}}^0$  is obtained which equals to  $-26.8 \text{ kJ mol}^{-1}$ .

The negative value of  $\Delta G_{\text{ads}}^0$  indicates the spontaneous inhibition of nitrite on the metal surface. In addition, the value of  $\Delta G_{\text{ads}}^0$  is around  $-20 \text{ kJ mol}^{-1}$  suggesting the electrostatic interaction between the nitrite and metal surface (physisorption) in 5 mM chloride solution at 25 °C.

## 4 | CONCLUSIONS

In this study, the inhibition mechanism of nitrite on the corrosion of carbon steel has been studied in a neutral solution with different concentrations of nitrite and chloride at different temperatures. The results obtained can be summarized as follows:

- The addition of nitrite up to 9 mM increases the inhibition efficiency while any further addition of nitrite has a negative effect on the corrosion performance. The corrosion state is in active dissolution at OCP regardless of the nitrite/chloride ions concentration ratio. However, a passivity state is attained when the chloride concentration is less than 5 mM at a high applied potential.
- The elevation of temperature from 25 to 65 °C increases dramatically the corrosion current density of carbon steel suggesting a significant reduction of nitrite inhibition.
- The increase of chloride concentration from 0 to 10 mM causes the significant increase in the corrosion current density and decrease in the pitting potential.  $E_{\text{pit}}$  depends on the chloride concentration according to a logarithm relation.
- The results obtained by the impedance measurements satisfy the polarization observations. Moreover, the analysis of impedance parameters shows that the inhibition mechanism of nitrite in the corrosion conditions of the present work is mainly processed through formation of the iron oxide layer of magnetite. Although, the probability of the formation of maghemite increases at high applied potential.
- The thermodynamic parameters indicated the monolayer adsorption on the carbon steel surface according to the Langmuir isotherm and the adsorption mechanism is mainly as physisorption process.

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