Synthesis and characterization of pH-responsive mesoporous chitosan microspheres loaded with sodium phytate for smart water-based coatings

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Funding information
National Science Fund for Distinguished Young Scholars, Grant number: 51525903; National Natural Science Foundation of China, Grant numbers: 51401185, 51709253, 51601188; Applied Basic Research Programs of Nantong, Grant number: GY12016002; Applied Basic Research Programs of Qingdao, Grant number: 17-1-1-98-jch; China Postdoctoral Science Foundation, Grant number: 2016M600563

Mesoporous micro- or nanocontainers have been indicated to be potential carriers of corrosion inhibitors to modify water-based coatings for self-healing properties and excellent anti-corrosion performance. In this work, the eco-friendly mesoporous chitosan microspheres loaded with green corrosion inhibitor sodium phytate were incorporated in self-healing water-based polyacrylate coating. The microspheres with mesoporous surface, uniform size, and promising pH responsiveness were prepared via the water-in-oil (W/O) emulsion chemical cross-linking method. On this basis, chitosan microspheres loaded with 25.79 wt% sodium phytate were obtained by negative pressure impregnation method and the pH-responsive was demonstrated by the electrochemical impedance spectroscopy (EIS). The results of EIS and seawater immersion tests revealed that artificial defected water-based polyacrylate coating containing 5 wt% chitosan microspheres showed high anti-corrosion performance and exhibited self-healing capabilities due to the release of corrosion inhibitor sodium phytate.

KEYWORDS
anti-corrosion, chitosan microspheres, pH-responsive, self-healing, water-based coating

1 | INTRODUCTION

Corrosion could seriously shorten the service life of metal and cause incredible economic losses. Organic coating system with simple operation, high cost performance, and excellent anti-corrosion performance is one of the most effective ways to protect the metal from corrosion. Epoxies, polyurethanes, and polyesters are all common organic coatings used on the surface of the metal, the core protective mechanism of which owes to the physical barrier. In addition, pigments and additives are normally added to the organic coatings to reach a more excellent protective effect. However, the emission of volatile organic compounds in the traditional solvent-based coatings could damage the environment and threaten the human health. In recent years, the current legislation levies have limited the use of these toxic compounds. So, the water-based coatings such as waterborne polyacrylate coating and waterborne polyurethane coating with low content of volatile organic compounds (VOC) have developed rapidly. Whereas, without special effective additive, the low level anti-corrosion protection is their main drawback. Furthermore, the residual hydrophilic components and the low cross-linking degree cause the weak barrier property against water, oxygen, and other...
corrosive species.\textsuperscript{[13]} So, effective measures should be adopted to improve the corrosion resistance and modify the barrier performance of the water-based coatings.

In recent years, researchers have proposed to add the host carriers encapsulated or loaded with corrosion inhibitors into the coatings to obtain self-healing ability and achieve an excellent anti-corrosion performance.\textsuperscript{[14]} When the coating failed, inhibitors would release from the containers, thus promoting a long-term anti-corrosion protection. The typical releasing mechanisms include moisture-induced expansion,\textsuperscript{[15]} local pH change,\textsuperscript{[16–20]} ion exchange,\textsuperscript{[21]} mechanical stress,\textsuperscript{[22]} water trapping, electrochemical potential change,\textsuperscript{[23,24]} and others. The common host carriers include organic polymeric microcapsules and inorganic micro- or nanocontainers. However, when polymeric microcapsules were used as containers, some problems still remained: 1) complicated synthesis process was needed\textsuperscript{[25]}, 2) toxic compounds were used in the synthesis process\textsuperscript{[26]}, 3) when the hydrophilic corrosion inhibitors such as sodium phytate and cerium ions were loaded using the common employed solvent evaporation method\textsuperscript{[27]} the low loading rate was caused by the hydrophilic nature of the corrosion inhibitors and hydrophobicity of the polymeric microcapsules. So inorganic nanocontainers were recently employed to host hydrophilic corrosion inhibitors.\textsuperscript{[28,29]} A new generation of mesoporous micro- and nanoparticles with high specific surface area has aroused great interest and been indicated as potential carriers of corrosion inhibitors.

Mesoporous microspheres based on chitosan show properties of non-toxicity, water-solubility, good biocompatibility,\textsuperscript{[30]} and pH-sensitivity. So they were commonly used as carriers to control the release of active agents in food industry\textsuperscript{[31]} and medical industry.\textsuperscript{[32,33]} However, to our knowledge, few researches have been reported to use green chitosan microspheres as carriers for corrosion inhibitors applied to improve the anti-corrosion effect of water-based coatings.

Sodium phytate is the sodium salt form of phytic acid and has been used as green corrosion inhibitor for copper.\textsuperscript{[34]} Moreover, sodium phytate could develop thick coating on the metal surface, thus improving the anti-corrosion performance of the coating. The sodium phytate solution was also used as medium to form anodic coatings on metal surface by the authors\textsuperscript{[35,36]} in order to prevent corrosion.

In this work, we reported the fabrication of eco-friendly mesoporous chitosan microspheres loaded with sodium phytate, for the first time, applied them in self-healing water-based polyacrylate coating. The microspheres were prepared via the via water-in-oil (W/O) emulsion chemical cross-linking method. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) were used to characterize the morphology of chitosan microspheres and thermogravimetric analysis (TGA) was used to analyze the load rate of sodium phytate. The chitosan microspheres were added into the water-based coating with the mass ratio of 5 wt% and the self-healing properties were studied by electrochemical impedance spectroscopy (EIS) and seawater immersion test.

## 2 | EXPERIMENTAL

### 2.1 | Materials

Plates of copper purchased from Xin Sheng Testing Center, China were used as substrates. Prior to use, all the substrates were sequentially treated with emery paper from 120 to 1000 grit. After rinsed in acetone for 10 min, the samples were cut into different sizes: 1 × 1 × 1 cm$^3$ for release kinetics and self-healing measurements; 5 × 10 × 0.5 cm$^3$ for seawater immersion test. Chitosan with 95% deacetylation degree was purchased from Shanghai Macklin Biochemical Co. Ltd. China. Sodium phytate and vanillin were supplied by Aladdin Industrial Corporation. Liquid paraffin, span 80 and acetic acid were obtained from Sinopharm Chemical Reagent Co. Ltd. China. All other chemical agents used were analytical grades.

### 2.2 | Synthesis of mesoporous chitosan microspheres

Chitosan microspheres were prepared via W/O emulsion chemical cross-linking method. Briefly, 100 mg chitosan was dissolved in 5 ml acetic acid solution (2%, v/v) to get a 20 mg/ml concentration. The mixture was stirred at room temperature with the speed of 1000 rpm until the chitosan was completely dissolved and then was used as water phase (W). Liquid paraffin (100 ml) with 2% span 80 as emulsifier was used as oil phase (O). Then the water phase (5 ml) was added to the oil phase (100 ml) drop by drop through an injector. After stirring at room temperature for 15 min, the NaOH solution (1 M) was added to adjust the mixture pH to 8–9. When the system was stable, vanillin dissolved in acetone with the concentration of 25 mg/ml (4, 8, 12, and 16 ml) was added drop wise to the W/O emulsion to cross-link chitosan for 5 h with constant stirring. Then, the chitosan microspheres were collected and sequentially washed by petroleum ether, acetone, and isopropanol. Finally, the microspheres were dried in a vacuum oven at 30 °C for 24 h.

Chitosan microspheres loaded with sodium phytate were prepared by negative pressure impregnation method. Briefly, 10 mg microspheres were added into sodium phytate solution (10%, w/w). When the mixture was blended well, the container of the mixture was transferred to a vacuum jar to conduct vacuum absorption, which was followed by washing with deionized water and centrifugation (4000 rpm). Finally, the precipitate was dried in a vacuum oven at 30 °C for 24 h.
The schematic diagram for preparation of chitosan microspheres loaded with sodium phytate is presented in Figure 1.

2.3 | Preparation of self-healing water-based polyacrylate coating

Conventional water-based polyacrylate coating was used as the initial system to prepare the self-healing anti-corrosion coating and as a reference in corrosion protection comparative test.

Coated samples were obtained by brushing the above-mentioned water-based coating doped with 0 or 5 wt% microspheres with the help of a wool brush. The thickness of dry coating was measured by EC-770 coating thickness gauge.

2.4 | Characterization of chitosan microspheres

The surface morphological characteristics of chitosan microspheres were examined by scanning electron microscope (Hitachi S4800, Japan). The samples were prepared by sprinkling microsphere powder on an adhesive tape mounted on a brass sample holder. Then, they were coated with gold powder and transferred to the sample chamber.

To explore the cross-linking mechanisms of chitosan microspheres, FT-IR spectra of the samples were measured by using FT-IR (Nicolet iS10, USA). Vanillin, chitosan, and chitosan microspheres were mixed with KBr. The spectra were acquired in the transmission mode in the range of 4000–400 cm⁻¹.

XRD measurements of chitosan and chitosan microspheres were obtained using an X-ray diffractometer (Ultima IV diffractometer, Japan). It was performed using Cu Kα radiation in the range (2θ) from 5 to 80° with a step of 0.02°.

To evaluate the load rate of sodium phytate in the microspheres, thermogravimetric analysis of samples were performed by thermal analyzer (Mettler TGA-DSC 1, Switzerland) with temperature range 50–800 °C, under N₂ atmosphere.

2.5 | Electrochemical measurements

2.5.1 | Release of corrosion inhibitor in aqueous media

The release kinetics of corrosion inhibitor from mesoporous microspheres was indirectly studied through examining the efficiency of the corrosion inhibitor by EIS. This method was referenced to Refs. [4,37,38]. The copper cube (1 × 1 × 1 cm³) samples were placed at 3.5% NaCl solution containing 0.5 wt % microspheres loaded with sodium phytate at various pH values (3.0, 7.0, and 9.0).

EIS measurements were performed by AUTOLAB 302N electrochemical system with a 10 mV peak to peak amplitude in frequency range from 10⁵ to 10⁻² Hz. A three-electrode system was used assembled with a saturated calomel reference electrode, a platinum plate counter electrode and the copper cube working electrode.

2.5.2 | Self-healing properties of the coating modified with microspheres

EIS was also used to evaluate the self-healing properties of the coated copper samples (1 × 1 × 1 cm³) with water-based coating (100 ± 5 µm thickness) doped with 0 or 5 wt% chitosan microspheres in 3.5% NaCl solution. A small circular defect (about 90 µm in diameter) was made on the surface of the coated samples to accelerate the corrosion process. The software Zview was used for analyzing EIS data by using suitable circuit models.
2.6 | Accelerated corrosion test

Copper test panels with dimensions of 5 × 10 × 0.5 cm³ were used for seawater immersion test. After rinsed in acetone, the dried samples were coated by a wool brush. The coated copper panels were prepared in three different types: Cu₁, coated with conventional water-based polyacrylate coating; Cu₂, coated with coating containing 5 wt% hollow chitosan microspheres; Cu₃, coated with the water-based coating doped with 5 wt% microspheres loaded with sodium phytate. Curing process was proceeded at room temperature for 7 days. Then, the copper panels were crosswise scribed 10 cm long by a sharp tool to accelerate corrosion process. Finally they were placed in the chamber filled with seawater, which was taken from the Bohai Sea. The duration of immersion test was set to test the corrosion resistance of the coating and lasted 90 days at 25 °C.

3 | RESULTS AND DISCUSSION

3.1 | Scanning electron microscopy

The morphology of mesoporous chitosan microspheres can be significantly influenced by the cross-linker consumption. Figure 2 shows the SEM images of chitosan microspheres with various volume of vanillin solution. Chitosan microspheres prepared with 4 and 8 ml vanillin solution were irregular in shape and even large blocking was observed. When 12 ml vanillin solution was used, the microspheres were in perfect sphere with uniform size ranging from 20 to 30 μm. Their surface was rugged with – micro-pores like,[39] which contributed to the release of the corrosion inhibitor. However, the microspheres with higher use amount of vanillin solution (16 ml) had obvious agglomeration. In the following experiment, we used 12 ml vanillin solution (25 mg/ml) to cross-link the chitosan microspheres.

3.2 | Fourier transform infrared spectroscopy

FT-IR spectra of vanillin, chitosan, and chitosan microspheres are shown in Figure 3. In FT-IR spectrum of vanillin
(Figure 3a), the peak at 3153 cm$^{-1}$ corresponded to the stretching vibration of $\sim$OH; while the absorption peak of bending vibration of $\sim$OH was at 1263 cm$^{-1}$. The peak at 1661 cm$^{-1}$ was attributed to the stretching vibration of C$\equiv$O; the absorption peak of stretching vibration of C$\sim$H was at 2861 cm$^{-1}$; the peaks at 1585, 1508, and 811 cm$^{-1}$ were the stretching vibration absorption peaks for the benzene ring. The FT-IR spectrum of chitosan is shown in Figure 3b. The band around 3360 cm$^{-1}$ corresponded to the overlapped stretching vibration of $\sim$OH and N$\sim$H; the absorption peak of stretching vibration of C$\sim$N was at 1375 cm$^{-1}$; the peak at 1590 cm$^{-1}$ corresponded to the bending vibration of $\sim$NH$_2$; the peak at 2868 cm$^{-1}$ was attributed to the stretching vibration of C$\sim$H; the absorption peak of stretching vibration of C$\sim$O in the ring of chitosan was at 1150 cm$^{-1}$; while the absorption peak of C$\sim$O in $\sim$CH$_2$$\sim$OH appeared at 1058 cm$^{-1}$. Figure 3c shows the FT-IR spectrum of the cross-linked chitosan microspheres. The peak appearing at 1584, 1496, and 822 cm$^{-1}$ indicated the presence of benzene ring in the cross-linked chitosan microspheres. The peak at 1643 cm$^{-1}$ was the stretching vibration absorption peak for C$\equiv$N, which was attributed to the Schiff base reaction between the $\sim$C$\equiv$O in vanillin and $\sim$NH$_2$ in chitosan. In addition, previous studies$^{[30]}$ have also reported similar results. The intensity of the absorption peaks at 2921 and 2861 cm$^{-1}$ corresponding to the stretching vibration of $\sim$CH$_3$ were obviously enhanced, which indicated the presence of $\sim$O$\sim$CH$_3$ group in the cross-linked chitosan microspheres. The absorption peak of $\sim$OH in chitosan shifted from 1263 to 1296 cm$^{-1}$ and the intensity of the absorption peak of C$\sim$O in $\sim$CH$_2$$\sim$OH at 1058 cm$^{-1}$ reduced, which confirmed the hydrogen bond interactions between vanillin and chitosan. This result also agreed with the previously published results.$^{[30]}$ According to the above analysis, the chitosan was cross-linked by vanillin through Schiff base reaction and hydrogen bond interaction. The possible cross-linking mechanism is presented in Figure 4.

![Cross-linking mechanism of chitosan with vanillin](image)

**FIGURE 4** Cross-linking mechanism of chitosan with vanillin

![XRD patterns of (a) chitosan and (b) chitosan microspheres cross-linked by vanillin](image)

**FIGURE 5** XRD patterns of (a) chitosan and (b) chitosan microspheres cross-linked by vanillin [Color figure can be viewed at wileyonlinelibrary.com]
3.3 | X-ray diffraction

Figure 5 shows the XRD patterns of chitoan and chitosan microspheres cross-linked by vanillin. It can be observed for chitosan there were two characteristic peaks at $2\theta = 20^\circ$ and $2\theta = 10^\circ$. Similar results have been published by Dan et al.\textsuperscript{[40]} In Figure 5b, the main peak for chitosan microspheres at $2\theta = 20^\circ$ was weakened and the peak at $2\theta = 10^\circ$ disappeared after they were cross-linked by vanillin. These results revealed that there were chemical bond cleavage and formation during the reaction process of chitosan with vanillin and the chitosan transformed from crystal to non-crystal under dehydration of acetone solution.\textsuperscript{[41]}

3.4 | Thermogravimetric analysis

Figure 6 shows the results of TGA measurements for corrosion inhibitor sodium phytate, hollow chitosan microspheres and microspheres loaded with sodium phytate. It revealed that there was hardly any weight loss of sodium phytate during the whole temperature rising process, indicating that sodium phytate was chemical stable and higher temperature was needed to decompose it. Owing to the evaporation of water and the depolymerization of chitosan, the obvious weight loss of chitosan microspheres could be obtained. The weight loss ratio of samples ($W$) is expressed as follows:

$$ W = \frac{m_1 - m_2}{m_1} \times 100\% $$

FIGURE 6  TGA curves of (a) sodium phytate, (b) chitosan, and (c) chitosan/sodium phytate [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 7  Nyquist plots (a), Bode impedance (b), and phase plots (c) of copper immersion in 3.5% NaCl solution containing 0.5% microspheres for different times at pH = 3 [Color figure can be viewed at wileyonlinelibrary.com]
where $m_1$ (mg) is the initial weight, $m_2$ (mg) represents the weight of samples after TGA measurement.

According to the formula, the weight loss ratio of sodium phytate, chitosan microspheres, and chitosan/sodium phytate were 0.64, 66.14, and 49.25 wt%, respectively, which were named $W_1$, $W_2$, $W_3$.

The load rate of sodium phytate ($\eta$) which refers to the overall mass of inhibitor with respect to the mass of chitosan/inhibitor together, was determined using Eq. (2):

$$W_3 = \eta W_1 + (1 - \eta) W_2$$  \hspace{1cm} (2)

According to Eq. (2), it could be calculated that the load rate of sodium phytate in microspheres was 25.79 wt%.

### 3.5 Release kinetics at different pH values

EIS measurements were used to evaluate the release kinetics of sodium phytate from chitosan microspheres. Copper electrodes were immersed in 3.5% NaCl solution with 0.5 wt% microspheres loaded with sodium phytate at pH = 3, 7, and 9.

Nyquist plots in Figure 7 show that the capacitive arc diameters gradually increased till 24 h during the immersion process at pH = 3. It indicated that the corrosion inhibitor sodium phytate was released from the mesoporous microspheres, leading to a higher charge transfer resistance. The results were further confirmed by Bode impedance Figure 7(b) and phase plots Figure 7(c). Both the impedance values at low frequency and phase angles ($\theta$) gradually increased as the immersion time elapsed from 0.5 to 24 h. Moreover, it also emphasized that the released corrosion inhibitor was absorbed on the copper surface forming a protective film.

Figure 8 illustrates the impedance diagrams obtained at pH = 7 during the immersion process. According to the Nyquist plots, it can be remarked that during the first 2 h immersion there was a smaller increase of the capacitive arc diameter. While the capacitive arc diameters significantly increased till reaching the maximum value, after 2 h immersion. The same behavior was confirmed by the Bode impedance and phase plots, which emphasized the corrosion inhibitor was apparently released from the microspheres after 2 h immersion and provided a more protective barrier film.

**FIGURE 8** Nyquist plots (a), Bode impedance (b), and phase plots (c) of copper immersion in 3.5% NaCl solution containing 0.5% microspheres for different times at pH = 7 [Color figure can be viewed at wileyonlinelibrary.com]
Estimating the Nyquist and Bode impedance for copper electrode at pH = 9 in Figure 9, the similar tendency to condition at pH = 3 and 7 was observed. In comparison to conditions at pH = 3 and pH = 9, capacitive arc diameters at pH = 9 were significantly increased, indicating that a greater amount of corrosion inhibitor was released from the microspheres.

Figure 10 summarizes the release kinetics of sodium phytate loaded microspheres in 3.5% NaCl solution at pH = 3, 7, and 9. The released corrosion inhibitor was absorbed on the copper electrode surface forming a protective film and the impedance modulus value of $|Z|_{0.01\text{ Hz}}$ at the frequency of 0.01 Hz represented the barrier properties of the film. Therefore, the ratio between $|Z|_{0.01\text{ Hz}}$ with microspheres and $|Z|_{0.01\text{ Hz}}$ without microspheres was chosen to evaluate the release of corrosion inhibitor. The value of $|Z|_{0.01\text{ Hz}}$ without microspheres can be regarded as the value of $|Z|_{0.01\text{ Hz}}$ with microspheres after 0.5 h immersion in NaCl solution, on account of negligible release of corrosion inhibitor for this short time.

In order to evaluate the corrosion inhibitor release kinetics, the following models were used to analyze the release data\cite{42}:

\begin{align*}
\text{Zero-order kinetics} & : \frac{M_t}{M_\infty} = kt \\
\text{First-order kinetics} & : \ln(1 - \frac{M_t}{M_\infty}) = kt
\end{align*}

Figure 10 Release kinetic curves of sodium phytate loaded chitosan microspheres in 3.5% NaCl solution at various pH [Color figure can be viewed at wileyonlinelibrary.com]
Korsmeyer-Peppas kinetics: \[ \ln\left(\frac{M_t}{M_\infty}\right) = n \ln t + \ln k \] (5)

where \( M_t/M_\infty \) is sodium phytate release fractions, in this work the ratio between \( |Z|_{0.01\ Hz} \) with microspheres and \( |Z|_{0.01\ Hz} \) without microspheres was used to replace \( M_t/M_\infty \) as drug release rate at time \( t \); \( k \) and \( n \) are corrosion inhibitor release constants.

The release parameters of corrosion inhibitor for these models are shown in Table 1. It is obvious that the best-fit model is Korsmeyer-Peppas model, since the correlation coefficients \( (r^2) \) were all greater than any other models. The release kinetic curves in Figure 10 were fitted using Korsmeyer-Peppas model. In addition, the release constant \( n \) was less than 0.43, which means the transport mechanism was fit for Fickian diffusion.[42]

Comparing the release kinetics of the chitosan microspheres under three different conditions at pH 3, 7, and 9, it can be concluded that the release rate of corrosion inhibitor was pH = 9 > pH = 7 > pH = 3. Because chitosan could be dissolved to be gel state and the transportation pores in the surface of the microspheres would be sealed at the condition of pH = 3, the release of corrosion inhibitor was slow. While, the microspheres were in a more stable state at the condition of pH = 9, and the interaction between the corrosion inhibitor protons and microspheres would be low, which caused a faster release.

**TABLE 1** Release parameters of Zero, First order, and Korsmeyer-Peppas models for sodium phytate release from chitosan microspheres

<table>
<thead>
<tr>
<th>pH</th>
<th>Correlation coefficient ( (r^2) ) Zero-order model</th>
<th>First-order model</th>
<th>Korsmeyer-Peppas model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( r^2 )</td>
</tr>
<tr>
<td>3</td>
<td>0.6694</td>
<td>0.4521</td>
<td>0.9475</td>
</tr>
<tr>
<td>7</td>
<td>0.7587</td>
<td>0.4817</td>
<td>0.9688</td>
</tr>
<tr>
<td>9</td>
<td>0.8817</td>
<td>0.6785</td>
<td>0.9877</td>
</tr>
</tbody>
</table>

**FIGURE 11** Impedance diagrams: Nyquist \((a_1,a_2)\) and Bode \((b_1,b_2)\) plots of samples with 0 and 5 wt% chitosan microspheres for the durability effect on the copper electrodes in 3.5\% NaCl solution [Color figure can be viewed at wileyonlinelibrary.com]
3.6 Corrosion performance of the coated samples

The EIS results of the samples coated with pure polyacrylate coating and coating containing 5 wt% chitosan microspheres after, 48, 96, 168, and 360 h immersion in 3.5% NaCl solution are presented in Figure 11. The Nyquist plots in both Figure 11(a1, a2) showed a depressed semicircle at high frequency, followed by a diffusion tail at low frequency (Warburg impedance). It indicated that the corrosion of copper in 3.5% NaCl was partly controlled by diffusion mass transport. Furthermore, with immersion time extending, the diameters of the semicircles at high frequency decreased in Figure 11(a1) but increased in (a2), indicating that the charge transfer resistance in Figure 11(a1) became smaller, while it became higher in (a2). Moreover, the tendency also emphasized that the barrier properties of coating without microspheres became worse but became better for the coating containing microspheres.

It could be seen from the Bode impedance Figure 11(b1) that the impedance values at the frequency 0.1 Hz (roughly reflecting the corrosion resistance of the coating) decreased with immersion time extending; while it increased in Figure 11(b2), reflecting that the released inhibitor plays a positive role in increasing the barrier properties of the coating.

For more accurate electrochemical behavior data of the coated samples during corrosion tests, the appropriate equivalent circuit was used to fit the EIS spectra. The Bode impedance and phase plots in Figure 11 showed two time constants for the both two coated samples. The general equivalent circuit \( R(QR)(Q(W)) \) is presented in Figure 12. \( R_{\text{sol}} \) refers to solution resistance; \( Q_{c} \) is constant phase element (CPE) of the polyacrylate coating; \( R_{po} \) is assigned to the resistance of the coating; \( Q_{dl} \) represents the constant phase element (CPE) of the double layer capacitance; \( R_{ct} \) is associated to the charge transfer resistance of the copper interface; \( W \) is the Warburg impedance. The impedance of a CPE is expressed as follows:

\[
Z_{\text{CPE}} = \frac{1}{Y_{0}(j\omega)^{-n}}
\]

where \( Y_{0} \) is the proportionality factor; \( j \) is the imaginary unit; \( \omega \) represents the angular frequency; \( n \) is a CPE exponent, which is close to 1 for an ideal capacitor. As a consequence

![FIGURE 12 Impedance spectrum fitting equivalent circuit diagram](image-url)

### Table 2

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>( R_{po} ) (Ω·cm²)</th>
<th>( R_{ct} ) (kΩ·cm²)</th>
<th>( Z_{0} (Q_{c}) ) (S s cm⁻²)</th>
<th>( Y_{0} (Q_{dl}) ) (S s cm⁻²)</th>
<th>( Y_{0} (W) ) (S s cm⁻⁰⁵)</th>
<th>( n_{c} )</th>
<th>( n_{dl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>892.9</td>
<td>64.850</td>
<td>64.850</td>
<td>64.850</td>
<td>64.850</td>
<td>64.850</td>
<td>64.850</td>
</tr>
<tr>
<td>48</td>
<td>903.8</td>
<td>77.300</td>
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<tr>
<td>96</td>
<td>946.2</td>
<td>86.130</td>
<td>86.130</td>
<td>86.130</td>
<td>86.130</td>
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of dispersing effect, the impedance spectra presented depressed semicircles rather than perfect semicircles. As electric double layer was deviating from pure capacitor, the CPE was used to fit the impedance.

The fitted data of the equivalent circuits are presented in Table 2. It is obvious that the \( R_{ct} \) of the coated samples containing sodium phytate loaded microspheres increased from 64.830 to 110.800 \( \text{k}\Omega \cdot \text{cm}^2 \) for 360 h immersion. It

**FIGURE 13** Results of the seawater immersion test for (a) pure water-based polyacrylate coating, (b) coating with 5 wt% hollow microspheres, and (c) coating with 5 wt% microspheres loaded with sodium phytate. From top to bottom: immersion for 0 day, 11 days, and 90 days [Color figure can be viewed at wileyonlinelibrary.com]
could be interpreted that the inhibitor sodium phytate was released from the internal channels of the mesoporous chitosan microspheres and was adsorbed on the surface of the copper electrode. In addition, the tendency agreed with the increase of the \( R_{po} \), indicating that the released inhibitor increased the barrier properties of the coating. At the same time, Warburg impedance decreased as the immersion time extended, reflecting the diffusion mass transport attenuated along with the adsorption of the inhibitor. As for the coated sample containing no microspheres, both the \( R_{c} \) and \( R_{po} \) decreased with the extending of the immersion time. The total impedance decreased from 105.300 to 9.035 k\( \Omega \cdot \text{cm}^2 \). It is reasonable to consider that as the immersion time went on, the electrolyte permeated into the coating and caused a negative effect on the barrier properties of the coating. However, \( R_{po} \) of the coating containing microspheres were all time lower than that of the no chitosan microspheres containing coating. Besides, the total impedance of the latter was higher than that of the former at the first 48 h immersion; while after 48 h immersion, the impedances of the sample containing microspheres were better. It could be assumed that the addition of microspheres caused the higher porosity of the coating, thus leading to the low \( R_{po} \). Nevertheless, with the increasing of immersion time, the inhibitor was leaked, which improved the charge transfer resistance as well as the barrier properties of the coating. Although the higher porosity caused by chitosan microspheres could not be neglected, in long-term, the addition of chitosan microspheres made the water-based polyacrylate coating transform into a considerable resistant coating.

3.7 | Seawater immersion test

The results of seawater immersion test are presented in Figure 13. Obviously, the pure water-based polyacrylate coating and coating containing 5 wt% hollow microspheres presented a corrosion attack around the defected area after immersion for 11 days and more serious deterioration of coupons could be seen after immersion for 90 days. It revealed that the hollow microspheres make no difference to anti-corrosion performance of water-based coating. However, the coating modified with sodium phytate loaded microspheres was free of rust after 11 days immersion in seawater and showed a better control of corrosion process even after 90 days immersion, which validated the self-healing properties of the water-based coating.

4 | CONCLUSIONS

Eco-friendly pH-sensitive mesoporous chitosan microspheres were successfully prepared via W/O emulsion chemical cross-linking method. The main findings can be drawn as follows:

1. The corrosion inhibitor sodium phytate was successfully encapsulated in the chitosan microspheres and the load rate was 25.79 wt%.
2. The pH-responsive property of the chitosan microspheres was demonstrated by EIS measurements. The results showed that the release rate of corrosion inhibitor was fastest at the condition of \( \text{pH} = 9 \) followed by the release rate at \( \text{pH} = 7 \) and \( \text{pH} = 3 \).
3. When the microspheres were added into the water-based coating, a significant increase of charge-transfer resistance could be obtained, indicating the self-healing capabilities of the modified coating.
4. The seawater immersion test revealed that the water-based coating modified with corrosion inhibitor loading chitosan microspheres could restrain corrosion process around defected areas, as a result of the release of corrosion inhibitor.

Therefore, water-based polyacrylate coating could transform into a considerable resistant coating with the addition of sodium phytate loaded chitosan microspheres.

ACKNOWLEDGMENTS

This research was jointly supported by the National Science Fund for Distinguished Young Scholars (No. 51525903); the National Natural Science Foundation of China (Nos: 51401185, 51709253, 51601188); Applied Basic Research Programs of Nantong (No. GY1201600); Applied Basic Research Programs of Qingdao (No. 17-1-1-98-jch); China Postdoctoral Science Foundation (No. 2016M600563).

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