Synergetic Anticorrosion Mechanism of Main Constituents in Chinese Yam Peel for Copper in Artificial Seawater

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ABSTRACT: Active constituents of Chinese yam peel (CYPE), namely, diosgenin (DOG), batatasin-I (BTS-I), batatasin-III (BTS-III), and yam polysaccharide (Y-PS), were extracted via an ultrasonic soaking strategy. The synergetic anticorrosion mechanism among these compounds for copper in artificial seawater (ASW) was clarified by gravimetric measurements, electrochemical evaluations, surface analyses, quantum chemical calculations under a dominant solvent model, and molecular dynamics (MD) simulations. The results of weight loss revealed that CYPE strongly inhibited the corrosion of copper in ASW, and the elevating temperature boosted the anticorrosion efficacy of CYPE. The inhibition efficiency could attain 96.33% with 900 mg/L CYPE in ASW at 298 K due to effective adsorption. CYPE simultaneously suppressed the anodic and cathodic reactions for copper in ASW, which could be categorized as the mixed-type corrosion inhibitor with the predominant anodic effect. Similar electrochemical kinetics was evidenced by electrochemical frequency modulation (EFM). Electrochemical impedance spectroscopy (EIS) indicated that CYPE prominently increased the charge-transfer resistance at the copper/electrolyte interface without altering the corrosion mechanism. Extending the immersion time was also conducive for CYPE to further minimize the corrosion of copper in ASW, which was demonstrated by the time-course polarization, EIS, and EFM tests. Owing to the adsorption of CYPE, the copper surface was well-protected and showed reduced wettability and limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness. From the outcomes of quantum chemical calculations, global and local reactive descriptors of DOG implied the cross-linked deposition of actually formed dioscin on the copper surface; otherwise, those of BTS-I/-III showed the limited variation of roughness.

1. INTRODUCTION

Corrosion is a detrimental and ubiquitous issue in many technological realms such as the marine industry, transportation, and electronic manufacturing, which immensely shortens the lifespan of metals (e.g., copper) and causes economic loss; therefore, it has been attracting numerous targeted investigations all along. Hitherto, persistent endeavors are engaged in impeding the metal corrosion, and many strategies have been developed such as appropriate structure design, electrochemical protection, application of coatings, and corrosion inhibitors. One of the beneficial methods to mitigate copper corrosion in aggressive media is the employment of corrosion inhibitors. Numerous synthetic compounds possessing heteroatoms (O, N and S, etc.), polar groups, and/or conjugated systems are specified as effective corrosion inhibitors for copper in diversified media. However, complicated synthesis routes and cost-ineffective products still hinder the actual application of as-fabricated inhibitors. Even worse, because of inherent toxicity, some effective compounds are hardly answerable as the eco-friendly solution for high-performance anticorrosion. Furthermore, severe environmental crisis has also urged researchers to develop efficient and high-performance corrosion inhibitors for copper in the aggressive media. Conforming with the sustainable awareness, commendable biomass-derived products as corrosion inhibitors possess salient advantages including biocompatibility, nontoxicity, and availability, to name just a few. Since the utilization of Chelidonium majus extract as a corrosion inhibitor in 1930, naturally occurring extracts have become a quickly growing family as an important green strategy for retarding the
unexpected metal dissolution in various corrosive environments. Typically, Ahmed and Zhang\textsuperscript{13} utilized the \textit{Atriplex leucoclad\textsubscript{a}} extract to inhibit copper corrosion in 1 M HCl solution, which behaved as a mixed-type inhibitor and adsorbed onto the substrate via monolayer assembly. They also prepared a bee pollen extract for copper corrosion in HCl solution;\textsuperscript{14} an anticorrosion efficiency of 94.5\% was attained with 7 g/L extract dosage. Hasanin and Al Kiey\textsuperscript{15} synthesized biopolymer nanocomposites based on extracted cellulose and niacin; the results of electrochemical and surface analyses indicated that the ethyl cellulose−niacin composite is the most effective product in mitigating the copper corrosion in 3.5\% NaCl solution, yielding an efficiency of 94.7\%.

Recently, extracting eco-friendly corrosion inhibitors from plant wastes has been attracting ever-increasing attention for the global appeal of garbage sorting and recycling.\textsuperscript{16} \textit{Chinese yam} (CYP) is a member of the genus \textit{Dioscorea}, whose rhizome is valued as food and for its medicinal properties.\textsuperscript{17} The peel of \textit{Chinese yam} (CYP) is usually pared and discarded as kitchen garbage before preparing cuisine due to its unpleasant flavor. Fundamentally, CYP possesses different phytochemical constituents (vide infra) of flavonoids, quercetins, and polyphenols which are active anticorrosion components, as reported by screening of common plant extracts.\textsuperscript{2,11,18−20} The anticorrosive capability and the underlying mechanism of the CYP extract (CYPE) have not been clarified for copper in aggressive media, especially the synergetic behavior among different constituents.

On that account, CYPE was acquired through the ultrasonic soaking method and characterized by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). Gravimetric, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and frequency modulation (EFM) were employed to evaluate the anticorrosive efficiency of CYPE for copper in artificial seawater (ASW). The effect of immersion time on the adsorption of CYPE at the copper/electrolyte interface was also estimated by time-course electrochemical protocols. Morphological observation, surface wettability, and three-dimensional topography consolidated the corrosion inhibition potency of CYPE. Quantum chemical calculations based on density functional theory (DFT) and molecular dynamics (MD) simulations were performed to authenticate experimental results.

2. RESULTS AND DISCUSSION

2.1. Characterization of CYPE. As reported elsewhere\textsuperscript{17,19,20} the phytochemical screening of CYPE showed that it contains diosgenin (DOG), batatasin-I (BTS-I), batatasin-III (BTS-III), and a yam polysaccharide (Y-PS), which are listed in Table 1. The verification of phytochemical constituents in CYPE was done by FTIR and XRD techniques, and the results are shown in Figure 1. For the FTIR spectrum

Table 1. Chemical Structures of Main Constituents in CYPE

| Constituents       | Structures                              |
|--------------------|-----------------------------------------|
| Diosgenin (DOG)    | ![Diosgenin Structure](image)           |
| Batatasin-I (BTS-I)| ![Batatasin-I Structure](image)         |
| Batatasin-III (BTS-III)| ![Batatasin-III Structure](image) |
| Yam polysaccharide (Y-PS)| ![Yam Polysaccharide Structure](image) |

(General formula)

![Figure 1. FTIR spectrum (a) and XRD pattern (b) of CYPE.](image)
of CYPE in Figure 1a, the broad absorption band centered at 3395 cm\(^{-1}\) is attributed to the stretching vibration of \(\text{OH}\) that stems from the terminal groups of all listed constituents in Table 1. The peak at 2928 cm\(^{-1}\) is associated with the stretching of aliphatic \(\text{C} - \text{C}/\text{C} - \text{H}\).4 The characteristic peak for unsaturated or conjugated \(\text{C}=\text{C}\) is identified at 1641 cm\(^{-1}\).21 The backbone breathing of benzene is found at the wide band centered at 1380 cm\(^{-1}\), on which the out-of-plane bending of \(\text{C} - \text{H}\) is recognized at 1019 cm\(^{-1}\).22 The peaks at 1158 and 1082 cm\(^{-1}\) are assigned to the stretching of two types of \(\text{C} - \text{O}\) groups; accordingly, the peak at 859 cm\(^{-1}\) is identified as the bending of the \(\alpha\)-glucosidic bond, that is, the typical characteristic of a natural polysaccharide.17 For the XRD pattern of CYPE displayed in Figure 1b, the diffractions at 14.82, 17.05, and 22.29° of 2\(\theta\) belong to the monoclinic and hexagonal crystal types of Y-PS, while those at 24.20, 26.48, and 38.04° are the typical diffractions of DOG crystalline.20 Crystallized Y-PS and DOG ensure their stability in the powder form, avoiding their condensation reaction after dissolution in the aqueous solution (vide infra). Also, the condensation between Y-PS and DOG could prevent the CYPE solution from converting into byproducts. In summary, FTIR and XRD analyses results are in good accordance with the compounds tabulated in Table 1.

2.2. Corrosion Resistance of CYPE for Copper in ASW.

2.2.1. Gravimetric Determination. Owing to the reliability and validity, the dynamic weight loss method was preferentially performed to ascertain the anticorrosion efficiency of CYPE for copper in ASW at all examined temperatures and concentrations. Figure 2 shows the variation of the corrosion rate (CR) and \(\text{IE}_w\) for copper in ASW without and with different CYPE concentrations at pre-set temperatures. It is clear from Figure 2a that the CR value increased with the elevation of temperatures and is hugely slowed down upon the addition of CYPE at a constant temperature. CYPE also exhibits a positive concentration effect on the corrosion mitigation of copper in ASW, that is, the CR value reduced progressively upon increasing the CYPE dosage. The concentration-/temperature-dependent CR indicates that copper was well-protected by CYPE through effective adsorption on the metal surface. Notably, when the CYPE concentration exceeds 900 mg/L, the change of CR is negligible. This may result from the dynamic equilibrium of CYPE adsorption/desorption at the copper/electrolyte interface.23 Figure 2b presents the variation of \(\text{IE}_w\) for copper in ASW in the absence and presence of different CYPE concentrations at the pre-set temperatures. At an arbitrary allocated temperature, \(\text{IE}_w\) increases with the augment of CYPE concentration and remains relatively stable or decreases slightly when the dosage of the inhibitor is over 900 mg/L. Interestingly, \(\text{IE}_w\) shows an upward trend with the elevated temperature at a constant CYPE concentration, which attains 96.33% for copper in ASW with 900 mg/L CYPE at 328 K. Considering the chemical activity of constituents in CYPE (Table 1), the condensation between DOG and Y-PS, as displayed in Figure 3,19 may account for the enhanced anticorrosion effect. In the saline solution, terminal hydroxyls on DOG are activated, which would be intensified as the temperature increases. The activated sites react with the grafted hydroxyl on the pyran unit of Y-PS, resulting in the formation of dioscin. Dioscin of high molecular weight tends to deposit on the copper surface, furthest covers the susceptible sites and increases the interfacial viscosity, which contribute to the improved \(\text{IE}_w\) with the elevation of temperature for copper in inhibited ASW. Meanwhile, other constituents (BTS-I and -III) can also adsorb at the uncover sites of the copper surface caused by the steric effect among dioscin chains, which promote the compactness and the uniformity of the adsorption layer.

Figure 2. CRs (a) and inhibition efficiencies (b) for copper in ASW with different concentrations of CYPE at the pre-set temperatures.

Figure 3. Schematic diagram of the condensation reaction between Y-PS and DOG.
Consequently, the synergy among the constituents of CYPE fortifies its corrosion inhibition effect for copper in ASW with increasing temperature. According to the optimal IE\textsubscript{w} value, 900 mg/L of CYPE was selected as the maximum concentration for latter analysis.

2.2.2. Adsorption Isotherm. The adsorption nature of an inhibitor on the metal surface can be revealed by various isotherms.\textsuperscript{24} Different adsorption models, for example, Langmuir, Temkin, Flory–Huggins, and Freundlich, were attempted to fit the gravimetric data. Thereinto, the Langmuir isotherm best describes the adsorption of CYPE onto the copper surface

\[
\theta = \frac{1 - \frac{C_{\text{inh}}}{K_{\text{ads}} + C_{\text{inh}}}}{100}
\]

where \(C_{\text{inh}}\) denotes the concentration of CYPE, mg/L; \(\theta\) denotes the surface coverage; and \(K_{\text{ads}}\) denotes the equilibrium constant of interfacial adsorption/desorption. Figure 4a shows the fitting results for CYPE adsorbed onto the copper surface. Evidently, all correlation coefficients \(R^2\) annotated in Figure 4a are close to unity, which validates the feasibility of the Langmuir model. In addition, the Langmuir isotherm assumes that all adsorption sites are energetically equivalent and thereby a monolayer inhibitor film forms on the copper surface without a lateral interaction among assembled molecules.\textsuperscript{23}

By employing Gibbs and van’t Hoff formulae (eqs 6a6a and 6b6b), thermodynamic parameters, namely, standard Gibbs free energy \(\Delta G_{\text{ads}}\) (kJ/mol), variation of enthalpy \(\Delta H_{\text{ads}}\) (kJ/mol), and variation of entropy \(\Delta S_{\text{ads}}\) (J/(mol·K)), are derived for CYPE adsorption on the copper surface.

\[
\Delta G_{\text{ads}} = -RT \ln(1000 \cdot K_{\text{ads}}) = \Delta H_{\text{ads}} - T \Delta S_{\text{ads}}
\]

where \(R\) is the universal gas constant, 8.314 J/(mol·K); \(T\) is the absolute temperature, K; and 1000 represents the mass concentration of an aqueous solution, g/L. The calculated \(\Delta G_{\text{ads}}\) values for the adsorption of CYPE on copper at 298, 308, 318, and 328 K are \(-22.22\), \(-23.18\), \(-24.58\), and \(-25.88\) kJ/mol, respectively. The negative sign of \(\Delta G_{\text{ads}}\) evidences the spontaneous adsorption of CYPE.\textsuperscript{25} Generally, \(\Delta G_{\text{ads}}\) up to \(-20\) kJ/mol or more positive is deemed physisorption triggered by Coulombic attraction and/or strong van der Waals interaction between the adsorbate and the metal substrate, while \(\Delta G_{\text{ads}}\) more negative than \(-40\) kJ/mol is usually categorized as chemisorption due to charge transfer and the subsequent formation of the covalent bond.\textsuperscript{22,26,27} The obtained \(\Delta G_{\text{ads}}\) values fall between \(-20\) and \(-40\) kJ/mol, indicating that physicochemical adsorption occurs for CYPE on the copper surface in ASW.\textsuperscript{28} A closer inspection on \(\Delta G_{\text{ads}}\) implies that CYPE is inclined to adsorb onto the copper surface in a physisorption manner for these values verging on \(-20\) kJ/mol. This may be assigned to the physical deposition of macromolecular dioscin. Moreover, the \(\Delta G_{\text{ads}}\) modulus increases with the augment of temperature, which can stem from the intensified interaction between BTS-I/-III and the copper surface. From the fitting results given in Figure 4b, \(\Delta H_{\text{ads}}\) and \(\Delta S_{\text{ads}}\) are calculated as 18.47 kJ/mol and 123.86 J/(mol·K), respectively, for CYPE adsorption on the copper surface. The positive sign of \(\Delta H_{\text{ads}}\) features the endothermic
Table 2. Kinetic Parameters of Copper after 1 h Immersion in ASW at 298 K without and with Different Concentrations of CYPE

| C_{CYPE} (mg/L) | E_{corr} (mV) | i_{corr} (μA/cm²) | β⁺ (mV/dec) | β⁻ (mV/dec) | IEp (%) |
|----------------|---------------|-------------------|-------------|-------------|---------|
| 0              | −255.64 ± 12.88 | 17.80 ± 3.63     | 86.76 ± 6.02 | 132.79 ± 9.87 |        |
| 100            | −250.85 ± 7.53  | 7.95 ± 1.52       | 95.86 ± 11.37 | 130.57 ± 9.87 | 55.34   |
| 300            | −243.56 ± 10.49 | 5.16 ± 0.97       | 97.33 ± 5.96  | 132.64 ± 12.05 | 71.01   |
| 500            | −230.13 ± 10.49 | 3.32 ± 1.43       | 100.21 ± 17.08 | 137.85 ± 18.13 | 81.35   |
| 700            | −219.32 ± 3.27  | 2.07 ± 1.04       | 107.22 ± 3.94  | 136.74 ± 2.73  | 88.37   |
| 900            | −219.38 ± 5.59  | 1.34 ± 1.04       | 111.97 ± 7.82  | 138.36 ± 11.56 | 92.47   |

Figure 6. Nyquist (a) and Bode (b) spectra for copper after 1 h immersion in ASW at 298 K without and with different concentrations of CYPE.

nature of the adsorption process, which explains the beneficial effect of increasing temperature on IE_p.29 Similar to the outcomes acquired by Keles et al.,26 the ΔH_ads value, herein, is in the range of 10–140 kJ/mol, in accordance with the complex physicochemical adsorption mechanism. Positive ΔS_ads means the aggravated irregularity after CYPE adsorption. As is known, water molecules are certainly superseded by CYPE, leading to the increase in interfacial disorder.30 Besides, irregular deposition of the macromolecular chain (dioscin) also boosts the disorder at the copper/electrolyte interface, thus yielding the positive ΔS_ads value.

2.2.3. Polarization Measurement. Figure 5a plots the evolution of E_{corr} with immersion time for copper in ASW at 298 K. Obviously, each sample achieves quasi-stability at the end of exposure. The equilibrium potential of the inhibited sample becomes nobler than that of uninhibited control, which is more distinct with the augment of the CYPE concentration. The effective adsorption of CYPE could shield the reactive sites on the copper surface and thereby elevate the value of E_{corr}.31 After 1 h immersion in the uninhibited and inhibited ASW, polarization curves for copper electrodes were recorded and are shown in Figure 5b. As is seen, almost overlapped cathodic branches reveal that the reduction mechanism of copper in ASW is unaffected in the presence of CYPE.32 It is thus anticipated that active cathodic sites are simply blocked by the geometric coverage of CYPE. On the contrary, the anodic branch is gradually suppressed by increasing the CYPE dosage, indicating that the anticorrosive effect of CYPE is predominately effectuated by the anodic inhibition.33

In light of the apparent linear portion of each curve in Figure 5b, Tafel extrapolation was performed to acquire kinetic parameters (Table 2), that is, corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic (β⁺) and cathodic (β⁻) Tafel slopes for quantitative evaluation of the inhibition efficiency of CYPE. From Table 2, it can be observed that E_{corr} shifts toward the positive direction with the augment of CYPE concentration; however, the maximum difference in E_{corr} is 36.32 mV that is less than 85 mV. Presumably, CYPE can be viewed as a mixed-type corrosion inhibitor with a dominant anodic effect for copper in ASW. This means that the adsorption of CYPE intensely retards the anodic dissolution process and simultaneously slows down the reduction at cathodic regions on the copper surface. The value of i_{corr} is dramatically reduced in the presence of CYPE and further decreases from 17.80 μA/cm² (without inhibitor) to 1.34 μA/cm² (900 mg/L CYPE). Therefore, CYPE efficiently slows the electrochemical corrosion of copper in ASW. The variation of IE_p derived from E_{corr} agrees well with that of IE_p, attaining 92.47% with the optimal concentration of CYPE. The neglectable difference among β⁻ values in Table 2 consolidates that CYPE possesses little effect on the cathodic reaction of copper exposed to ASW.34 Conversely, β⁺ gradually enlarges from 86.76 mV/dec (without CYPE) to 111.97 mV/dec (900 mg/L CYPE), implying that the anodic dissolution of copper in ASW is efficiently retarded by the adsorption of CYPE.

2.2.4. Electrochemical Impedance Spectroscopy. Figure 6 shows the EIS data of copper electrodes after 1 h immersion in ASW without and with different concentrations of CYPE at 298 K. Nyquist spectra in Figure 6a exhibit the similar shape, indicating that the presence of CYPE in ASW hardly alters the corrosion mechanism of copper. Besides, the predominant capacitive loop across almost the whole frequency range of each curve corresponds to interfacial charge transfer and double layer behaviors, which also reveals that CYPE controls copper corrosion primarily through the effective adsorption.35 The curvature diameter of the Nyquist semi-circle is prominently larger for the inhibited sample as compared to that of blank control, and it progressively increases with increasing CYPE concentration. The enlarged Nyquist loop signifies the enhanced charge-transfer resistance due to the gradual uniformity of the adsorption layer across the copper/solution interface.36 The increased interfacial resistance by...
employing CYPE is also evidenced by Bode spectra shown in Figure 6b. The low-frequency impedance of the Bode modulus increases with the increase of the CYPE concentration. Meanwhile, the slope of the linear portion in the intermediate-frequency region is close to unity, implying the preferred capacitive behavior at the copper/electrolyte interface due to the compact adsorption layer.\(^3\) Another aspect, the maximum of the Bode phase angle increases with the increase of the CYPE concentration prompts\(^n\) the 2.2.5 Electrochemical Frequency Modulation. Unlike kinetic parameters from the accelerated mode in polarization tests, EFM is capable of generating relevant outcomes in a non-destructive manner.\(^4\) Figure S1 illustrates the EFM spectra of copper electrodes after 1 h immersion in ASW without and with different concentrations of CYPE at 298 K. The current responses in Figure S1 at both harmonic and intermodulation frequencies are more conspicuous than the background noise validating the rationality of data. Thus, the proposed circuits. As is observed, \(R_t\) increases as the CYPE concentration increases, revealing that the compact barrier layer is anchored on the copper surface in the presence of CYPE.\(^5\) Moreover, \(R_s\) considerably boosts from 1.32 (blank) to 20.42 k\(\Omega\)·cm\(^2\) when the CYPE concentration reaches 900 mg/L. The reinforced \(R_s\) discloses the attenuation of mass/electron transfer along the outer Helmholtz plane at the copper/electrolyte interface; in other words, the corrosion of copper in ASW is significantly slowed by the efficient adsorption of CYPE. In turn, through the adsorption of inhibitor, \(C_{dl}\) decreases to 11.40 \(\mu\)F/cm\(^2\) with the optimal CYPE dosage, which can be explained by the Helmholtz model\(^5\)

\[
C_{dl} = \frac{\varepsilon_f}{d} S 
\]

where \(\varepsilon_f\) and \(\varepsilon_s\) are the dielectric constants of air and the local adsorbed layer, respectively; \(d\) is the thickness of the double layer; and \(S\) is the geometric area of the exposed copper surface. The adsorption of CYPE necessarily lowers the local dielectric constant and increases the double layer thickness at the copper/electrolyte interface. Therefore, \(C_{dl}\) decreases for copper immersed in the inhibited ASW. Besides, the increasing CYPE concentration prompts \(n_t\) and \(n_{dl}\) values to approach unity, which is also attributed to the decline of interfacial heterogeneity due to inhibitor adsorption.\(^2\) The improved protection efficiency is also evidenced by the diminishing diffusion behavior (\(W\)) with increasing CYPE concentration of the intact adsorption layer formed with a high dosage of inhibitor.

2.2.5. Electrochemical Frequency Modulation. Unlike assessing kinetic parameters from the accelerated mode in polarization tests, EFM is capable of generating relevant outcomes in a non-destructive manner.\(^4\) Figure S1 illustrates the EFM spectra of copper electrodes after 1 h immersion in ASW without and with different concentrations of CYPE at 298 K. The current responses in Figure S1 at both harmonic and intermodulation frequencies are more conspicuous than the background noise validating the rationality of data. Thus, the proposed circuits. As is observed, \(R_t\) increases as the CYPE concentration increases, revealing that the compact barrier layer is anchored on the copper surface in the presence of CYPE.\(^5\) Moreover, \(R_s\) considerably boosts from 1.32 (blank) to 20.42 k\(\Omega\)·cm\(^2\) when the CYPE concentration reaches 900 mg/L. The reinforced \(R_s\) discloses the attenuation of mass/electron transfer along the outer Helmholtz plane at the copper/electrolyte interface; in other words, the corrosion of copper in ASW is significantly slowed by the efficient adsorption of CYPE. In turn, through the adsorption of inhibitor, \(C_{dl}\) decreases to 11.40 \(\mu\)F/cm\(^2\) with the optimal CYPE dosage, which can be explained by the Helmholtz model\(^5\)

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Table 3. Impedance Parameters of Copper after 1 h Immersion in ASW at 298 K without and with Different Concentrations of CYPE

| CYPE (mg/L) | \(R_t\) (\(\Omega\)·cm\(^2\)) | \(Q_t\) | \(n_t\) | \(R_{dl}\) (k\(\Omega\)·cm\(^2\)) | \(Q_{dl}\) | \(W\) (\(\Omega\)·cm\(^{-1/2}\)) | \(I_E\) (%) | \(\chi^2\) (x10\(^{-3}\)) |
|-------------|-----------------|--------|--------|-----------------|--------|--------------------|--------|-------------|
| 0           | 155.39          | 28.09  | 0.55   | 1.32            | 106.52 | 0.73               | 4.57   | 103         |
| 100         | 187.64          | 22.41  | 0.62   | 3.75            | 75.39  | 0.76               | 3.12   | 64.80       |
| 300         | 189.91          | 18.57  | 0.60   | 5.78            | 58.01  | 0.81               | 1.01   | 77.16       |
| 500         | 205.23          | 17.33  | 0.73   | 8.67            | 32.49  | 0.81               | 0.68   | 84.78       |
| 700         | 239.79          | 15.85  | 0.68   | 11.82           | 15.86  | 0.83               | 88.83  | 0.93        |
| 900         | 237.44          | 13.17  | 0.77   | 20.42           | 11.40  | 0.85               | 93.54  | 3.52        |
coupled with the impedance characteristics presented in Figure 6, an activation-controlled mode was employed to calculate the kinetic parameters. The fitted results, namely, the corrosion current density ($i_{corr}$), causality factors (CF2 and CF3), and anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes, are summarized in Figure 8. In Figure 8a, CF2 and CF3 close to the ideal magnitudes (2 and 3, respectively) indicate the satisfactory causality between the input frequency perturbation and the signal response. Similar to the results derived from polarization measurements, $i_{corr}$ persistently declines with the increase in CYPE concentration due to the constituent adsorption at the copper/electrolyte interface. In Figure 8b, $i_{corr}$ is reduced to 1.811 $\mu$A/cm$^2$, when the concentration of CYPE attains 900 mg/L, yielding the highest IEf. In addition, the indistinct variation of $\beta_c$ implies the unaffected cathodic reduction mechanism for copper in ASW with increasing CYPE dosage. On the contrary, $\beta_a$ gradually augments as the concentration of CYPE increases, indicating that the anodic dissolution of copper is efficiently hindered. The kinetic parameters derived from EFM spectra possess almost the same features as the counterparts acquired from polarization curves. In summary, the evolutions of IEf, $i_{corr}$, $\beta_a$, and $\beta_c$ are mutually consistent with the variation of the CYPE concentration. Ultimately, it is rational to conclude that CYPE can spontaneously adsorb onto the copper surface, retard the anodic dissolution, and thus inhibit the copper corrosion in ASW effectively.

2.3. Time-Course Anticorrosion Efficiency of CYPE.

2.3.1. Potentiodynamic Polarization. Considering that dioscin of high molecular weight could be formed during the immersion process, the effect of exposure time on the anticorrosive efficiency of CYPE was further evaluated for copper in ASW to verify the postulated adsorption nature (vide supra). Figure 9a shows the relationship between $E_{ocp}$ and immersion periods for copper in ASW with 900 mg/L CYPE at 298 K. The stabilized $E_{ocp}$ becomes nobler as the immersion time increases from 1 to 12 h. On the one hand, prolonging the exposure duration favors the deposition and relaxation of the dioscin chain at the copper/electrolyte interface; subsequently, the adsorption layer is strengthened and furthest covers the active sites on the metal surface. On the other hand, BTS-I and -III tend to chemically adsorb onto the copper surface, which is deemed a time-dependent process. Therefore, long-term immersion promotes the sufficient anchoring of BTS-I and -III at the gaps uncovered by dioscin, which synergistically generate the homogeneous and compact adsorption layer with the augment of immersion time. By virtue of the intact CYPE layer on the copper surface, $E_{ocp}$ necessarily elevates as the immersion time increases. The enhanced adsorption layer on the copper surface after long-term immersion is also manifested by polarization determinations (Figure 9b). In Figure 9b, both anodic and cathodic branches shift toward a low current density region as the immersion time is prolonged. Notably, an apparent passivation phenomenon is observed at about 0.02 V for copper after 8 h immersion in the inhibited solution. With further extension of the exposure period to 12 h, a lower passivation potential emerges at $-0.09$ V, inferring a better protective layer formed on the copper surface. Through Tafel extrapolation, the kinetic parameters for copper after different immersion times in ASW with 900 mg/L CYPE were calculated and are presented in Figure 10.
The long-term immersion evidenced by nearly unchanged shown in Figure 9b. Hence, an exposure time of 8 h is immersion is almost the same as that with 8 h exposure, as addition, the passivity current density of the specimen after 12 h increases as the time is prolonged. Therefore, it is clear in Bode spectra that the extension of exposure time for copper in the inhibited ASW favors the compaction of the CYPE layer.

Equivalent circuits depicted in Figure 7 were also adaptable for EIS spectra in Figure 10, and the acquired parameters are listed in Table 5. Specifically, Figure 7a matches well with the spectrum of copper after 2 h immersion in the inhibited ASW for the faint diffusion phenomenon at the low-frequency region; the other circuit (Figure 7b) is suitable for the residual spectra. The low magnitude of $\chi^2$ values in Table 5 confirms the validity of the fitting procedures. As is observed, relatively stable $R_e$ and $C_P$ values reveal the equilibrium interfacial state of copper with the optimal concentration of CYPE in ASW. On the contrary, the $R_i$ value increases from 20.42 kΩ·cm² (1 h) to 25.73 kΩ·cm² (8 h) for copper in ASW with 900 mg/L CYPE, which quantitatively demonstrates the enhanced corrosion-resistant layer. Further extending the exposure time (12 h) has little effect on the anticorrosive behavior of CYPE for the competitive $R_{ct}$ value with that of the specimen after 8 h immersion. Due to the effective adsorption of CYPE, the CYPE were acquired and are tabulated in Table 4. Clearly, $E_{corr}$ continuously shifts to the positive direction, indicating the reduced corrosion-susceptibility for copper in ASW. According to Table 4, $i_{corr}$ decreases from 1.34 μA/cm² (1 h) to 0.68 μA/cm² (8 h), yielding a high IEp value as 96.18%. This reveals that increasing immersion time further slows the corrosion rate of copper in ASW. Apparently, an exposure period of 12 h exhibits little improvement of the lowering $E_{corr}$ value. In addition, the passivity current density of the specimen after 12 h immersion is almost the same as that with 8 h exposure, as shown in Figure 9b. Hence, an exposure time of 8 h is adequate for copper in the inhibited ASW. The anodic and cathodic corrosion mechanisms are hardly influenced during the long-term immersion evidenced by nearly unchanged $\beta_a$ and $\beta_c$.

Figure 10 displays the EIS spectra of copper after different immersion times in ASW with 900 mg/L CYPE at 298 K. For the Nyquist spectra shown in Figure 10a, a similar shape of the capacitive loops for diversified samples consolidate the same corrosion mechanism for copper in ASW (i.e., controlled by charge transfer) with different concentrations of CYPE. Extending the immersion time from 1 to 8 h enlarges the diameter of the Nyquist curve, indicating the increased impedance modulus for charge transfer. Besides, the span of the capacitive loop for the sample after 8 h immersion is more completed between $10^{-2}$ and $10^5$ Hz than those with less exposure duration. This articulates the uniform and homogeneous adsorption layer formed on the copper surface. Especially, the capacitive loop for copper after 12 h immersion almost overlaps with that after 8 h exposure in the inhibited ASW, consolidating that an integrated adsorption layer had been formed on the copper surface. Likewise, as a semi-quantitative indicator of the anticorrosive efficacy, the low-frequency resistance ($R_{corr}$) presented in the Bode modulus (Figure 10b) augments with increasing immersion time. Furthermore, the maximum of the phase angle also gradually elevates as the time is prolonged. Therefore, it is clear in Bode spectra that the extension of exposure time for copper in the inhibited ASW favors the compaction of the CYPE layer.

Table 4. Kinetic Parameters of Copper in the Inhibited ASW (900 mg/L CYPE) with Different Immersion Times at 298 K

| time (h) | $E_{corr}$ (mV) | $i_{corr}$ (μA/cm²) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | IEp (%) |
|---------|-----------------|---------------------|-------------------|-------------------|---------|
| 1       | $-219.38 \pm 5.59$ | $1.34 \pm 1.04$    | $111.97 \pm 7.82$ | $138.36 \pm 11.56$ | 92.47   |
| 2       | $-214.43 \pm 7.36$ | $1.08 \pm 0.95$    | $113.59 \pm 15.36$ | $136.85 \pm 17.01$ | 93.93   |
| 4       | $-210.79 \pm 2.46$ | $0.97 \pm 0.73$    | $109.21 \pm 11.64$ | $139.02 \pm 5.44$ | 94.55   |
| 8       | $-210.82 \pm 9.23$ | $0.68 \pm 0.19$    | $111.40 \pm 9.98$ | $135.97 \pm 12.07$ | 96.18   |
| 12      | $-208.77 \pm 4.19$ | $0.69 \pm 0.35$    | $105.29 \pm 18.01$ | $133.29 \pm 9.39$ | 96.12   |

Table 5. Impedance Parameters of Copper after 1 h Immersion in the Inhibited ASW (900 mg/L CYPE) with Different Immersion Times at 298 K

| time (h) | $R_e$ (Ω·cm²) | $C_P$ (μF/cm²) | $n_f$ | $R_i$ (kΩ·cm²) | $Q_f$ | $C_d$ (μF/cm²) | $n_d$ | $W$ (Ω·cm²·s⁻¹) | IEp (%) | $\chi^2$ (×10⁻⁵) |
|---------|--------------|---------------|-------|---------------|--------|---------------|-------|----------------|---------|-----------------|
| 1       | 237.44       | 13.17         | 0.77  | 20.42         | 11.40  | 0.85          | 93.54 | 5.34           | 94.28   | 0.94            |
| 2       | 240.15       | 14.02         | 0.69  | 21.82         | 11.23  | 0.85          | 93.95 | 3.03           | 94.87   | 1.46            |
| 4       | 239.64       | 12.89         | 0.65  | 23.06         | 10.48  | 0.86          | 94.28 | 0.94           | 94.87   | 1.46            |
| 8       | 233.75       | 12.57         | 0.70  | 25.73         | 10.35  | 0.88          | 94.87 | 1.46           | 94.87   | 2.12            |
| 12      | 255.10       | 12.50         | 0.69  | 25.75         | 11.01  | 0.91          | 94.87 | 2.12           | 94.87   | 2.12            |
capacitive feature of the double layer at the copper/electrolyte interface is deteriorated leading to the decline of $C_{dl}$ values. Sufficient CYPE adsorption also generates a smooth and uniform copper surface that is documented by the increasing $n_{dl}$ value with the augment of immersion time.

EFM was also conducted to probe the evolution of kinetic parameters as a function of immersion time. Figure S2 displays the EFM spectra for copper after different immersion times in the inhibited ASW (900 mg/L) at 298 K. Employing the activation-controlled mode, kinetic parameters were derived and are illustrated in Figure 11. CF2 and CF3 values given in Figure 11a are close to the ideal magnitudes 2 and 3, respectively, which validates the accuracy of measurements.40 As expected, $i_{corr}$ shown in Figure 11a is reduced with the extension of immersion time, revealing the suppressed copper corrosion by the fortified CYPE layer; in turn, the $IE_{f}$ value in Figure 11b increases as time prolongs achieving as 95.59% after 8 h immersion in the inhibited ASW. In addition, the histograms of $\beta_i$ and $\beta_c$ show an inconspicuous change with the augment of immersion time, which indicates that anodic and cathodic reaction mechanisms are invariable on the addition of CYPE for copper in ASW. Based on the electrochemical analyses of time effect on the anticorrosive capacity of CYPE, it can be highlighted that prolonging the immersion time ensures the integrity and uniformity of the adsorbed layer on the copper surface.

2.4. Surface Characteristics. 2.4.1. Surface Morphology and Wettability. Morphological observation can intuitively distinguish the anticorrosive effect of an inhibitor for metals in corrosive media. Optical textures, microstructures, and surface wettability (inset) of different copper specimens are presented in Figure 12. A shining appearance is observed in Figure 12a for the freshly polished sample. Deservedly, a flat morphology is presented in Figure 12b, in which scratches caused by mechanical grinding are clearly seen. A dominant content of the Cu element and a faint O content for a freshly polished specimen in Table 6 suggest the uncorroded copper surface. The water contact angle of the polished sample is measured as 55.6°, inferring a hydrophilic property. On the contrary, for the specimen after 72 h immersion in the uninhibited ASW, the copper surface is tarnished instead by the diffused rusty spots, as shown in Figure 12c. Meanwhile, plentiful pits and crevices
are seen in Figure 12d caused by severe corrosion, which is also supported by the elevated O content on the copper surface (Table 6). Due to the capillary effect of a deteriorated surface,45,46 the water contact angle of the corroded sample is lowered to 38.3°. In sharp contrast to Figure 12c, a well-protected surface is shown in Figure 12e, which furthest retains the primal gloss of copper compared with that imaged in Figure 12a. Similarly, a uniform and intact appearance of the copper surface is presented in Figure 12f, indicating that corrosion is efficiently minimized by the adsorption of CYPE. Beneﬁting from the effective adsorption of low-polarity organic constituents, the contact angle attains 88.9° for the inhibited sample. Notably, the presence of C element reveals the adsorption of CYPE on the copper surface; moreover, the relatively high content of O element may be ascribed to the deposited dioscin containing a Y-PS moiety. The element mapping of the inhibited copper surface (Figure 12g–i) strongly demonstrates the adsorption of CYPE on the copper surface. The uniform distributions of C and Cu elements, respectively, in Figure 12g,i reveal the effective adsorption of CYPE on the copper surface along with the well-protected copper surface. Whereas the relatively agglomerated O element in Figure 12h is assigned to the hydroxyls on adsorbed species and faint copper oxidation. The dense adsorption layer as evidenced by surface analysis greatly prohibits or delays the contact between the corrosive species and the copper surface, which facilitates the favorable anticorrosion capability of CYPE.

2.4.2. Surface Topography. AFM is a powerful tool to delineate the surface topography in a micro-/nanoscale, for which the anticorrosive effect is easily distinguished for an inhibitor. Figure 13 shows the three-dimensional surface topographies of different copper specimens along with the corresponding average roughness ($r_a$). In Figure 13a, the freshly polished sample exhibits a ﬂat topography, in which parallel grooves resulting from polishing are clearly observed. It is found in Figure 13b that the $r_a$ value of the polished sample achieves 103.2 nm. On the contrary, an extremely rugged topography with many humps and valleys is seen in Figure 13c for the specimen after 72 h of immersion in ASW without CYPE. The corresponding $r_a$ value reaches up to 476.9 nm (Figure 13d), indicating that the copper surface is seriously corroded in the uninhibited ASW. By contrast, the topography in Figure 13e is considerably improved for copper after 72 h of immersion in ASW with 900 mg/L CYPE. Expectably, the $r_a$

Table 6. Contents of Typical Elements on the Copper Surface after 72 h Immersion in ASW at 298 K without and with 900 mg/L CYPE along with the Freshly Polished Specimen for Comparison

| sample                        | element | atomic concentration (%) |
|-------------------------------|---------|--------------------------|
| freshly polished              | Cu      | 96.40 ± 2.03             |
|                               | O       | 2.57 ± 0.49              |
| uninhibited                  | Cu      | 82.16 ± 5.03             |
|                               | O       | 11.93 ± 6.04             |
| inhibited with 900 mg/L CYPE | C       | 3.52 ± 1.33              |
|                               | O       | 8.05 ± 2.06              |
|                               | Cu      | 88.28 ± 6.04             |

Figure 13. Three-dimensional topographies (left) and height proﬁle (right) of copper specimens after 72 h of immersion in ASW at 298 K: (a,b) freshly polished, (c,d) without CYPE, and (e,f) with 900 mg/L CYPE.
value is reduced to 199.3 nm (Figure 13f) for the adsorption of CYPE, which weakens the hazardous damage of corrosive species toward the copper surface.

2.5. Theoretical Simulation. 2.5.1. Global Reactive Descriptors. To afford deep insights into the reactivity of main constituents in CYPE, quantum chemical calculations were conducted based on DFT. Initially, it is of necessity to perform the microspecies analysis on each component in CYPE in a full pH range to ascertain its specific chemical state. Based on both convenient and economic standpoints, Y-PS and the resulting dioscin of high molecular weight were not involved in theoretical analysis. Instead, DOG, along with BTS-I and -III, was representatively analyzed, from which the actual deposition behavior of dioscin could be estimated. Figure S3 provides the microspecies distributions of DOG, BTS-I, and BTS-III. In light of the determined pH of ASW (~7.38), three constituents keep the neutral state in the corrosive solution. Therefore, neutral molecules of these compounds were engaged in the corresponding dominant solvent models and the subsequent DFT calculations.

Global reactive descriptors, namely, the optimized structure, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) distributions of DOG, BTS-I, and BTS-III are visualized in Figure 14. In general, Frontier molecular orbitals reflect the reactive activity of an inhibitor. Particularly, HOMO denotes the electron-donating tendency of the inhibitor, while LUMO measures the tendency of a molecule accommodating electrons. In the case of DOG, HOMO concentrates on the 1,6-dioxaspiro[4.5]-decane structure, as depicted in Figure 14b. The exchange of electron density between HOMO and the surrounding solvent reveals the strong electron-donating tendency of this moiety on DOG, which shows the propensity of chelating with cuprous/cupric ions and the subsequent deposition at the copper/electrolyte interface. The LUMO of DOG is mainly distributed on the cyclohexanol group, designating the position of electron

Figure 14. Optimized structure (left), HOMO (middle), and LUMO (right) distributions of DOG (a–c), BTS-I (d–f), and BTS-III (g–i) in dominant solvent models.

Figure 15. Number of condensed atoms (upper) and dual Fukui indices (lower) for DOG (a,d), BTS-I (b,e), and BTS-III (c,f) calculated using the respective dominant models.
Figure 16. Top and side snapshots of the equilibrium adsorption configurations for DOG (a), BTS-I (b), and BTS-III (c).

acceptance for accomplishing the condensation with Y-PS (Figure 3). For BTS-I, HOMO in Figure 14e spreads over the whole molecular backbone, while LUMO in Figure 14f exhibits a similar distribution except for the two methyl ether terminals. Regarding BTS-III, HOMO in Figure 14h is primarily distributed on the 3-methoxyphenol moiety, and the other portion contributes to the LUMO distribution, as illustrated in Figure 14i. Furthermore, both the HOMO and LUMO of BTS-III possess a strong reaction tendency toward the ambient chemisorption on the copper surface.39

2.5.2. Local Reactive Descriptors. Local reactive parameters, such as Fukui indices \( f_k^+ \) and \( f_k^- \), can be utilized to define the crucial reactive sites on an inhibitor.49 The functions \( f_k^+ \) and \( f_k^- \) are related to nucleophilic and electrophilic susceptibilities, respectively, which are defined as

\[
\begin{align*}
    f_k^+ &= q_k(N + 1) - q_k(N) \\
    f_k^- &= q_k(N) - q_k(N - 1)
\end{align*}
\]

where \( q_k(N + 1) \), \( q_k(N) \), and \( q_k(N - 1) \) represent the atom \( k \) in cationic, neutral, and anionic states, respectively. Herein, we introduced the dual Fukui function \( \Delta f_k \) to accurately locate the nucleophilic and electrophilic sites on target molecules, which is expressed as

\[
\Delta f_k = f_k^+ - f_k^-
\]

The number of condensed atoms and the corresponding values of \( \Delta f_k \) (denoted by Mulliken charge) for DOG, BTS-I, and BTS-III are summarized in Figure 15. As explained by Lgaz et al.,50 the positive \( \Delta f_k \) implies the electrophilic nature of an atom, while the negative counterpart signifies the nucleophilic center. In Figure 15d, C5–C7 on DOG exhibit a strong nucleophilic activity for accepting electrons. Besides, O13 and O18 are prominently electrophilic sites, which can donate surplus electrons toward the substrate. As for BTS-I (Figure 15e), nucleophilic centers are found on C2, C5, C9, C14, and O15, while the electrophilic sites are evenly spread over C1, C4, C6, C8, C11−C13, O16, and O20. It is clear in Figure 15f that the nucleophilic and electrophilic sites are separately located on the respective molecular terminal of BTS-III. In detail, C3−C8 and O9 possess nucleophilic activity; another aspect, C11−12, C14−15, O16, and O18 play a key role in electrophilic attack. A further comparison between Figures 14 and 15 features that the local active centers of DOG, BTS-I, and BTS-III are coincidently derived from the corresponding global Frontier molecular orbital distributions.

2.5.3. MD Simulations. MD simulations were conducted to clarify the adsorption mechanism of DOG, BTS-I, and BTS-III on the Cu(110) plane along with the respective interaction \( E_{\text{inter}} \) and binding \( E_{\text{bind}} \) energies. The fluctuations of temperature and energies for the simulation courses are shown in Figure S4, from which substantial equilibrium can be observed for each adsorption process. The equilibrium adsorption configurations of DOG, BTS-I, and BTS-III on the Cu(110) plane are illustrated in Figure 16. According to the side view in Figure 16a, DOG adsorbs onto the copper surface in an aslant manner with the main body (containing the reactive site with Y-PS) stretching into the bulk solution. It can be inferred from this orientation that the actually existent dioscin chains are probably cross-linked on the copper surface. In Figure 16b, a parallel configuration is found for the adsorption of BTS-I from both top and side snapshots. A similar adsorption orientation is observed in Figure 16c for BTS-III on the Cu(110) plane. The parallel adsorption configuration is conducive to BTS-I and BTS-III to sufficiently cover the active sites on the copper surface, which thereby isolates the substrate from corrosive attack in ASW. In addition, the anchoring of BTS-I and -III can fill the exposed sites that are unprotected by dioscin, synergistically enhancing the anticorrosive efficacy of CYPE.

The calculated \( E_{\text{inter}} \) values for DOG, BTS-I, and BTS-III adsorbed onto the Cu(110) plane are \(-389.91, -787.33, \) and \(-735.40 \) kJ/mol, respectively. The negative sign of \( E_{\text{inter}} \) signifies the simultaneous adsorption of inhibitors on the copper surface,28 which has been verified by thermodynamic analysis (Section 2.2.2). In turn, the \( E_{\text{bind}} \) values are \( 389.91, 787.33, \) and \( 735.40 \) kJ/mol for DOG, BTS-I, and BTS-III, respectively, indicating that the three compounds exhibit a strong anchoring preference toward the copper surface.51 In spite of the inferior molecular weight, BTS-I and BTS-III possess a larger magnitude of \( E_{\text{bind}} \) than that of DOG. This may stem from their superior adsorption configuration on the copper substrate.

2.6. Proposed Anticorrosion Mechanism. According to the correlated experimental and theoretical assays, the anticorrosive mechanism of CYPE for copper in ASW is proposed in Figure 17. DOG, BTS-I, and BTS-III preferentially adsorb onto the copper surface and exert a fast corrosion inhibition capacity, as evidenced by gravimetric and electro-
chemical determinations. Therein, the condensed reaction between DOG and Y-PS would be intensified by increasing the temperature and/or immersion time and thus yield dioscin of high molecular weight. Subsequently, dioscin could be physically deposited at the copper/electrolyte interface in a cross-linked manner. Meanwhile, BTS-I and BTS-III are chemically anchored on the metal substrate by virtue of their favorable reactive descriptors and preferred adsorption configuration, which are confirmed by theoretical simulations. As a result, the adsorption layer becomes compact and uniform by the synergistic behavior among the main constituents in CYPE. Additionally, benefiting from the pronounced proportion of macromolecules (dioscin), the apparent $\Delta G_{ads}$ approaches $\sim 20 \text{ kJ/mol}$ as acquired from thermodynamic calculations. Extending the immersion time avails BTS-I and BTS-III to further fill the unprotected voids, which enhances the synergetic effect with dioscin. In addition, the synergy of BTS-I and -III is regarded as a time-dependent process, as documented by time-course electrochemical evaluations. Owing to the synergistic anticorrosion effect among DOG, BTS-I, and BTS-III, the charge exchange on the copper surface is highly suppressed resulting in a well-protected substrate in ASW.

3. CONCLUSIONS

Efficient corrosion inhibitors were extracted from Chinese yam peel (CYPE) through the ultrasonic soaking strategy in ethanol for copper in ASW. The anticorrosive effect of CYPE was confirmed by complementary experimental and theoretical investigations. The remarkable conclusions are compiled as follows.

(i) CR value of copper in ASW was significantly reduced upon the addition of CYPE due to spontaneous adsorption; thus, $\text{IE}_{\text{w}}$ continuously increased with the augment of CYPE concentration. Elevating temperature enhanced the anticorrosive capacity of CYPE, the optimal $\text{IE}_{\text{w}}$ value reached 96.33% with 900 mg/L CYPE at 328 K. The adsorption of CYPE on the copper surface conformed with the Langmuir isotherm with endothermic and entropy increasing features.

(ii) CYPE behaved as a mixed-type corrosion inhibitor with dominant anodic retardation that hugely suppressed the $i_{\text{corr}}$ value. Non-destructive EFM measurements consolidated the kinetic properties of copper corrosion in ASW. According to EIS data, the $R_{\text{ct}}$ value was progressively reinforced in the presence and with the increase in the CYPE concentration, yielding the favorable protection toward the substrate. A prolonged immersion time was conducive to improving the anticorrosive efficiency, as observed from electrochemical inspection on the time effect.

(iii) The presence of CYPE furthest retained the glossiness of copper after 72 h of immersion in ASW at 298 K; and few deteriorated signs were seen on the micrograph of the metal surface. Due to the effective adsorption of CYPE, the water wettability of the copper surface was reduced, which could isolate corrosive species from contacting the substrate. The protected copper surface maintained the flat topography with a limited increase in $r_{\text{af}}$ as compared to the freshly polished counterpart.

(iv) The pervasive and polarized distributions of global/local descriptors for the respective BTS-I and BTS-III facilitated their parallel adsorption on the Cu(110) plane in a chemical form, while DOG favored the physical adsorption on the copper surface, indicating a cross-linked orientation after being condensed with Y-PS.

In summary, this work may provide meaningful implications for developing green corrosion inhibitors from environmental waste and pave a potential alternative way to address the degradation problem of copper-based facilities (e.g., electronic devices) in the marine environment.

4. EXPERIMENTAL SECTION

4.1. Materials. CYP was collected from the Planting Base of Tieguan Chinese yam in Jiaozuo, Henan Province (China) in October 2020. Anhydrous ethanol, NaCl, MgCl$_2$, Na$_3$SO$_4$, CaCl$_2$, KCl, NaHCO$_3$, KBr, H$_2$BO$_3$, SrCl$_2$, and NaF were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents were of analytical pure grade and utilized as received. T1 copper sheets (purity: 99.9%) with the dimension of 50 $\times$ 25 $\times$ 2 mm$^3$ were supplied by GRINM Group Co., Ltd. (China). Lab-made ultrapure water (18.5 MΩ-cm$^{-2}$) was used to prepare all solutions and for physical cleaning. Especially, ASW was prepared according to the description in ASTM D1141-98 (2013), as summarized in Table S1 (Supporting Information).

4.2. Extraction Procedure and Characterization. CYP was cleaned with water to remove dust, oven-dried at 338 K for 12 h, and sieved by a 100-mesh sifter. An ultrasonic soaking extraction protocol was performed to obtain CYPE. In detail, a given amount of dried CYP was added to a 1000 mL round-bottom flask with excessive anhydrous ethanol, which was transferred in an ultrasonic (100 kHz) water bath at 348 K for 72 h under reflux condensation. Afterward, the ethanolic mixture was naturally cooled, centrifuged at 5000 rpm/4600 rcf for 15 min, and the sediment was pipetted off, leaving the supernatant for vacuum-drying until a pale-yellow solid was formed (yield: 38.75%).

The solid compound was pulverized into fine particles for posterior studies. FTIR spectra (Nicolet iN10 model, Thermo Scientific, USA) were used to verify the typical structures of these compounds in a wavenumber from 4000 to 400 cm$^{-1}$. The condensed phase of CYPE was clarified by XRD (Panalytical X’Pert powder, the Netherlands) using Cu K$\alpha$ radiation operated at 40 kV with the 2$\theta$ range from 5 to 90° and a step size of 0.1°.

4.3. Corrosion Inhibition Evaluation. 4.3.1. Gravimetric Method. Copper sheets were initially degreased in ethanol,
washed with ultrapure water, abraded consecutively with SiC papers ranging from 200# to 2000#, ultrasonicated in an ethanol bath to remove debris and finally dried under blowing nitrogen. Accurately weighed sheets, in triplicate, were mounted on RCC-III rotating corrosion equipment (Qinyou Company, China), which were immersed in ASW with different concentrations of CYPE at selected temperatures for 72 h at a rotating speed of 72 rpm. Thereafter, the tested specimens were taken out, cleaned via the standard protocol given in ASTM G1-03 and reweighed until successive values agreed to the difference less than 0.2 mg. According to the mass variation of copper (Δm, mg) before and after immersion in ASW, the corrosion rate (CR, mm/a) and the corresponding inhibition efficiency (IE, %) were calculated using the following equations

$$\text{CR} = \frac{\Delta m \times 8.76}{A \times t} \times 100\% \quad \text{(8a)}$$

$$\text{IE} = \frac{\text{CR}_0 - \text{CR}}{\text{CR}_0} \times 100\% \quad \text{(8b)}$$

where A is the area of the copper specimen, mm²; t is the immersion period in the unit of year; and CR₀ and CR are the corrosion rates for specimens in the uninhibited and inhibited ASW, respectively.

4.3.2. Electrochemical Test. Copper sheets were incised into small pieces (10 × 10 × 2 mm³), which were sealed by polyethylene resin leaving a single surface and underwent the same polished protocol, as defined in gravimetric tests. Electrochemical studies were performed in a three-electrode cell using an Autolab PGSTAT302N workstation at 298 K, which assembled with the copper working electrode, the reference electrode (Ag/AgCl(s)), and the counter electrode (platinum foil, 1 cm²). Initially, working electrodes were conditioned in ASW for 30 min to stabilize the open-circuit potential (Eocp). Potentiodynamic polarization was performed for copper after various immersion times in ASW without and with different concentrations of CYPE. The potential range versus Eocp was from −0.25 to 0.35 V with a scan rate of 0.5 mV/s. Based on the fitted corrosion current density (iCorr μA/cm²), the inhibition efficiency (IEcorr, %) was evaluated as follows

$$\text{IE}_{corr} = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100\% \quad \text{(9)}$$

where iCorr₀ and iCorr are the corrosion current densities of copper after immersion in the uninhibited and inhibited ASW, respectively. EIS was registered at Eocp in a frequency domain from 10³ to 10⁻² Hz with an AC sine wave amplitude of 10 mV. Based on the fitted charge-transfer resistance (Rct, Ω cm²), the inhibition efficiency (IEct, %) could be estimated by the following relationship

$$\text{IE}_{ct} = \frac{R_{ct}^0 - R_{ct}}{R_{ct}^0} \times 100\% \quad \text{(10)}$$

where Rₜ₀ and Rₜ are the charge-transfer resistances of copper after immersion in the uninhibited and inhibited ASW, respectively. Electrochemical kinetics of copper exposed in ASW was also non-destructively clarified by the EFM technique. Measurements were conducted at a base frequency of 0.1 Hz using the multipliers of 2 and 5 for 16 cycles with the perturbation signal of 10 mV. Each electrochemical test was repeated three times for the representability of outcomes, and the aforementioned fitting processes were achieved through Nova 2.1 software.

4.3.3. Surface Analysis. The surface states of copper before and after 72 h of immersion in ASW at 298 K were examined by a DSX 1000 OLYMPUS digital microscope (Japan) under the same luminous conditions along with the freshly polished counterpart. The corresponding surface morphologies were imaged via a QUANTA FEG 250 scanning electron microscope (FEI, USA); the elemental analysis was realized by the attached energy-dispersive X-ray spectrometer (OCTANE PRIME model, AMETEK Inc.). An OCA 35 contact angle goniometer (Dataphysics, Germany) was utilized to determine the water wettability of different copper samples through the sessile drop configuration at 298 K. Three-dimensional topographies of different specimens were recorded using a Dimension FastScan atomic force microscope (Bruker, Germany) in the tapping mode. Triplicate spots (each area: 30 × 30 mm²) were randomly selected, and the average topography was adopted after being analyzed by Nanoscope 1.8 software.

4.4. Computational Study. 4.4.1. Quantum Chemical Calculations. Considering the actual service condition of CYPE, dominant solvent models, similar to those in our previous studies, were initially built for DOG, BTS-I, and BTS-III in ASW.⁵,²²,⁴¹ Thereupon, quantum chemical calculations based on DFT were completed through the DMol³ package of Materials Studio (BIOVIA Inc., France). Each model was fully optimized using the B3LYP functional. An all-electron double-numerical atomic orbital augmented by d-polarization (DNP, version 4.4) was applied as the basis set. After executing the energy task, global reactive descriptors of three systems, that is, the optimized structure, HOMO, and LUMO, were acquired. Noticeably, unlike the prevalent analyzing protocols in other literature,⁴¹,⁴₂,⁴₃ it is difficult to compare the specific reactive parameters among different dominant models, such as the HOMO/LUMO energies, energy gap, electronegativity, and dipole moment, since the inherent eigenvalues were inevitably affected by the electronic properties of the existing solvent layer. Besides, Fukui indices as the local reactive descriptors were also calculated under the same parameters’ setting as those employed in the acquisition of global counterparts.

4.4.2. MD Simulations. The ground-state structures of DOG, BTS-I, and BTS-III optimized in an electronic scale were used as the initial configuration for MD simulations. The Cu(110) plane with the highest surface energy was selected and cleaved (five layers) as the studied surface for its maximum tendency of accommodating adsorbates among other lattice planes,⁵ which was frozen during simulation. Considering the applied “fine” accuracy, the supercell was enlarged as 14 × 14 with a vacuum thickness of 30 Å, and a periodic box of 39.1 × 43.5 × 41.6 Å³ was built to fulfill simulations. As per the components in practical ASW, the formula of the simulated solution is proposed in Table S2 besides the single inhibitor molecule. Each system for inhibitor adsorption on Cu(110) was initially optimized under the self-developed ab initio force field (InterfaceFF) involving both physical and chemical interacting considerations. A dynamic simulation of 2000 ps (0.5 fs time step) was conducted under an NVT canonical ensemble (constant particle number, system volume, and temperature maintained at 298 K by the Nose—Hoover thermostat) to probe the equilibrium of configuration and energies of a specific constituent on the Cu(110) plane. $E_{water}$
and $E_{\text{bind}}$ of each target inhibitor were derived from the average equilibrium of last 100 ps as per the expression

$$E_{\text{inter}} = E_{\text{total}} - (E_{\text{Cu+electrolyte}} + E_{\text{inh}}) = -E_{\text{bind}} \quad (11)$$

where $E_{\text{total}}$, $E_{\text{Cu+electrolyte}}$ and $E_{\text{inh}}$ are the energy of the entire system, the system without an inhibitor, and the sole inhibitor, respectively, in kJ/mol.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04500.

- List of the components of ASW and the periodic box in MD simulations; EFM spectra of copper after 1 h immersion in ASW without and with different concentrations of CYPE and after different immersion periods in ASW with 900 mg/L CYPE; microparticles analyses; and temperature/energy equilibrium in MD simulations for DOG, BTS-I, and -III (PDF)

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### Notes

The authors declare no competing financial interest.

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