

Article

Insights into the Adsorption Mechanism and Corrosion Protection of Phytic Acid Conversion Coatings on Fe, Cu, and Al Surfaces: A Combined Theoretical and Experimental Study

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Abstract

This study explores the surface interaction mechanism of phytic acid (PA) on Fe, Cu, and Al metals and its applicability in green anticorrosion surface treatment through a combination of quantum chemical calculations, molecular dynamics (MD) simulations, and electrochemical measurements. Quantum chemical calculations identified the nucleophilic/electrophilic active sites of PA via HOMO-LUMO and Fukui functions. MD simulations then constructed solution-metal interface models, calculating adsorption energies, radial distribution functions, and the diffusion behavior of H₂O and Cl[−] to elucidate PA's adsorption configurations and its inhibition of corrosive species diffusion. Based on these theoretical insights, PA conversion coatings were in situ constructed on Fe, Cu, and Al substrates. Potentiodynamic polarization tests confirmed that these coatings effectively enhanced the corrosion resistance of the metals in a 3.5 wt% NaCl solution, achieving inhibition efficiencies of 92% for Fe, 86.5% for Al, and 26% for Cu. This work provides a comprehensive mechanistic interpretation from molecular adsorption to surface film formation, offering theoretical and experimental support for PA-based green surface treatment technologies.

Keywords: phytic acid; metal corrosion; quantum chemical calculation; molecular dynamics; electrochemistry



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1. Introduction

Metal corrosion is a ubiquitous electrochemical deterioration process that critically constrains modern industry and materials science, causing annual economic losses of approximately 3%–5% of global GDP [1–6]. To address corrosion in atmospheric [7], aqueous [8] and industrial media [9], corrosion inhibition research has become a major focus in materials chemistry, especially for the energy, construction, marine and aerospace sectors that heavily rely on iron-based [10], copper-based [11,12] and aluminum-based [13,14] materials.

Among existing protection strategies, corrosion inhibitors offer simple application, low cost, and good adaptability [15–17]. However, traditional chromate and phosphate

inhibitors contain heavy metals and persistent toxic substances, and they are facing increasing environmental restrictions [18,19]. Chemical passivation, which forms a dense passivation film (e.g., chromate conversion coating) on the metal surface to physically block corrosive media, also suffers from pollution, complex procedures, and limited universality across metals. Against this backdrop, developing renewable, eco-friendly systems that combine inhibition and film-forming capabilities is highly desired [20,21].

Phytic acid (PA) [22], a natural, eco-friendly, water-soluble compound abundant in plant seeds [23], possesses six phosphate groups that confer strong chelating ability and multiple active sites [24–27]. Its adsorption, film-forming, pH-responsive and biocompatible properties make it promising for corrosion protection. Kaghazchi et al. [28] examined the synergistic corrosion inhibition between PA and Zn^{2+} in 3.5 wt% NaCl. They confirmed that the chelate formed by PA and Zn^{2+} deposits on mild steel, providing enhanced protection. Separately, Li et al. [29] first employed an electrolysis method to prepare PA conversion films on copper foil, demonstrating that films formed under an applied electric field exhibit superior corrosion resistance. Shi et al. [30] studied an environmentally friendly PA conversion coating on 2024-T3 aluminum alloy. The coating was prepared in PA solutions with pH values ranging from 3 to 5.5, and characterized by SEM, EDS, ATR-FTIR, and electrochemical tests. The results indicate that the film formed within this pH range provides excellent corrosion resistance.

Despite these advances, most studies rely on macroscopic electrochemical tests or static surface characterization [31–33], failing to reveal the dynamic evolution of adsorption configurations, stability, and film formation kinetics at the atomic/molecular scale. Given the wide applications of Fe, Cu, and Al in fields such as construction, marine industry, and aerospace, where they are exposed to similar corrosive environments [34–37], this paper systematically investigates the adsorption thermodynamics, kinetics, and structure—activity relationship of PA molecules on the surfaces of metals Fe, Cu, and Al through quantum chemical calculations and molecular dynamics simulations. PA conversion films are then prepared by a controlled immersion method, and their long-term protective performance in 3.5 wt% NaCl is quantitatively evaluated by electrochemical polarization. The findings provide both theoretical and experimental support for a chromium-free, low-toxicity, scalable PA-based anticorrosion technology.

2. Calculation Method and Materials

2.1. Quantum Chemical Calculations

Quantum chemical calculations can effectively predict the chemical reactivity of molecules and are widely used in structure-activity relationship studies of corrosion inhibitors. In this work, the Gaussian 09 software package [38] was employed, utilizing the B3LYP functional combined with the 6-311G++(d,p) basis set to perform geometry optimization, obtaining the most stable molecular conformation on the potential energy surface. The electronic structure of the optimized PA molecule was then analyzed and visualized using Multiwfn [39,40], developed by Lu et al. [41], and Visual Molecular Dynamics (VMD) [42]. The highest occupied molecular orbital energy (E_{HOMO}) and the lowest unoccupied molecular orbital energy (E_{LUMO}) were obtained from the calculations. Other quantum chemical descriptors based on E_{HOMO} and E_{LUMO} , such as the energy gap (ΔE), electronegativity (χ), chemical potential (μ), hardness (η), and softness (S), were calculated using the following formulas:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

$$\mu = -\chi = \frac{E_{LUMO} + E_{HOMO}}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (3)$$

$$S = \frac{1}{\eta} \quad (4)$$

To analyze the local reactivity of PA molecules, the electrostatic potential and Fukui functions of the molecule were calculated. The Fukui function $f(\vec{r})$ is defined as the first partial derivative of the electron density $\rho(\vec{r})$ with respect to the number of electrons N .

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{v(\vec{r})} \quad (5)$$

Using the finite difference approximation, the Fukui function $f(\vec{r})$ can be expressed as:

$$f^+(\vec{r}) = q(N+1) - q(N) \quad (6)$$

$$f^-(\vec{r}) = q(N) - q(N-1) \quad (7)$$

Here, $q(N+1)$, $q(N)$, and $q(N-1)$ represent the atomic charges in systems with electron numbers $N+1$, N , and $N-1$, respectively. These indices reflect the propensity of an atom to gain or lose electrons. A larger f^+ value indicates a stronger ability of the atom to gain electrons, suggesting it is more susceptible to nucleophilic attack. Conversely, a larger f^- value signifies a stronger tendency of the atom to lose electrons, implying it is more prone to electrophilic attack.

2.2. Molecular Dynamics Simulations

Molecular dynamics (MD) simulations were performed using the Forcite module in the Materials Studio 2020(MS) software package. In this study, the relatively stable Fe(110), Cu(111), and Al(111) surfaces were selected as substrates for the simulations. Four solution models were constructed using the Amorphous Cell module, with their compositions and designations summarized in Table 1.

Table 1. Physical properties and components of the solution models.

Solution Type	Density ρ (g/cm ³)	Num. of Water Molecules (n_w)	Num. of PA Molecules (n_{PA})	Num. of Cl ⁻ Ions (n_{Cl^-})	Num. of Na ⁺ Ions (n_{Na^+})
Pure water	1.000	1000	0	0	0
PA	1.021	1000	3	0	0
NaCl	1.025	1000	0	11	11
NaClPA	1.030	1000	3	11	11

A three-layer periodic adsorption model was constructed by combining the solution with the metal substrate: the first layer consisted of the metal, the second layer comprised the solution, and the remaining region was set as the vacuum layer, as shown in Figure 1.

Atomic and molecular interactions were described using the COMPASSIII force field. As an ab initio force field, COMPASS [43] can predict properties of both gaseous and condensed phases, making it suitable for a wide range of organic and inorganic systems. It allows for the unified treatment of different material systems and provides reasonable descriptions of their mixtures. Geometry optimization of the initial model was performed by sequentially applying the steepest descent and conjugate gradient methods. The metal

substrate was kept fixed throughout the optimization, with a maximum of 10^5 iterations. Molecular dynamics simulations were performed using the optimized initial model, with the atoms in the top two layers of the metal substrate released. The simulations were conducted under the NVT ensemble at room temperature (298 K) for a duration of 2000 ps to allow the adsorption model to reach an equilibrium state. During MD simulations, fluctuations in temperature and energy within 5% to 10% of their average values typically indicate that the system has achieved equilibrium. Figure 2 shows that both temperature and energy fluctuations in the system remain within this range, indicating that a simulation duration of 2000 ps is sufficient for the system to reach equilibrium.

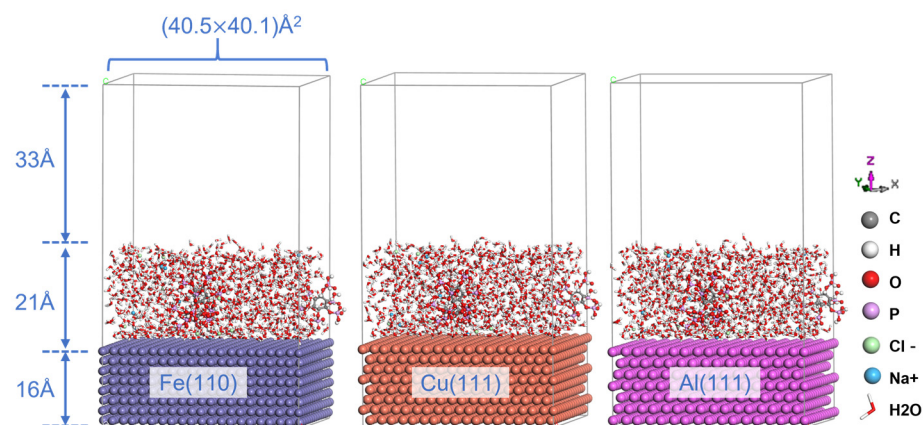


Figure 1. Establishment of the adsorption model.

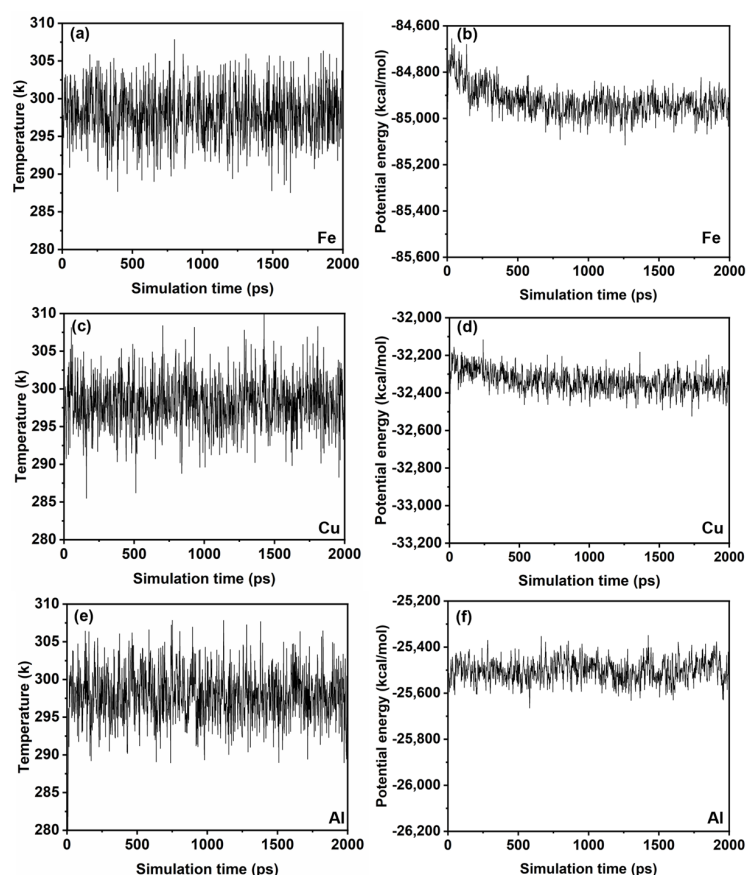


Figure 2. (a,c,e) Temperature and (b,d,f) energy evolution during MD simulations for Fe, Cu, and Al, respectively.

The MD simulations were performed with a time step of 1 fs and a cutoff radius of 12.5 Å. The atom-based method was employed for van der Waals interactions, while the Ewald method was used for electrostatic interactions. The Andersen thermostat and Berendsen barostat were selected for temperature and pressure control, respectively.

2.3. Experimental Materials

The substrate materials were high-purity metal discs (99.99% purity) of Fe, Cu, and Al, with a diameter of 15 mm and a thickness of 2 mm. Chemical reagents: phytic acid solution ($C_6H_{18}O_{24}P_6$, PA, 50 wt%), sodium chloride (NaCl), and sodium hydroxide (NaOH) were all supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China).

Prior to modification, all metal substrates were ground with SiC abrasive paper (400 to 1200 mesh) and polished to a mirror finish. The polished samples were then degreased by ultrasonication in acetone, absolute ethanol, and deionized water for 10 min each, followed by natural drying.

A 1 wt% PA working solution was obtained by diluting the as-received 50 wt% PA solution with deionized water, and its pH was adjusted to 6.0 by dropwise addition of NaOH solution.

The cleaned metal samples were immersed in this PA solution for 1 h at ambient temperature, subsequently rinsed with deionized water for 60 s, and finally dried in air for 10 min.

A 3.5 wt% NaCl solution was also prepared for subsequent corrosion tests.

2.4. Electrochemical Testing

The corrosion behavior of bare and PA-treated Fe, Cu, and Al samples was evaluated by potentiodynamic polarization in a 3.5 wt% NaCl solution ($pH \approx 6.8$) at room temperature (25 ± 1 °C) using an electrochemical workstation (Corrtest CS2350M, Wuhan, China). A conventional three-electrode setup was employed, which consisted of a saturated calomel reference electrode, a platinum auxiliary electrode, and the test sample as the working electrode. Before each measurement, the open-circuit potential was recorded for 30 min to ensure the system's stabilization.

Polarization curves were then obtained by sweeping the potential from -0.5 V to 1 V vs. SCE at a scan rate of 1 mV/s, with the area of the working electrode fixed at 0.5 cm². The corrosion current density and corrosion potential were derived from the polarization curves using the Tafel extrapolation method.

2.5. Film Composition and Morphology Characterization

The surface morphology and elemental composition of Fe, Cu, and Al samples before and after treatment were characterized using a field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscope (EDS) (JSM-IT500, Tokyo, Japan). Fourier transform infrared spectroscopy (FTIR) (NICOLET5700FT-IP, Waltham, MA, USA) was employed to identify the functional groups of the conversion films formed on the metal surfaces.

3. Results and Discussion

3.1. Quantum Chemical Calculation of PA Molecule Activity

Figure 3a displays the fully optimized geometry of the PA molecule at the B3LYP/6-311G++(d,p) level. The corresponding electrostatic potential (ESP) map is shown in Figure 3b. ESP mapping visualizes the charge distribution across the molecular surface, with blue and red regions denoting negative (electrophilic) and positive (nucleophilic) po-

tential areas, respectively. The fitted ESP values range from a minimum of -45.93 kcal/mol to a maximum of 82.14 kcal/mol.

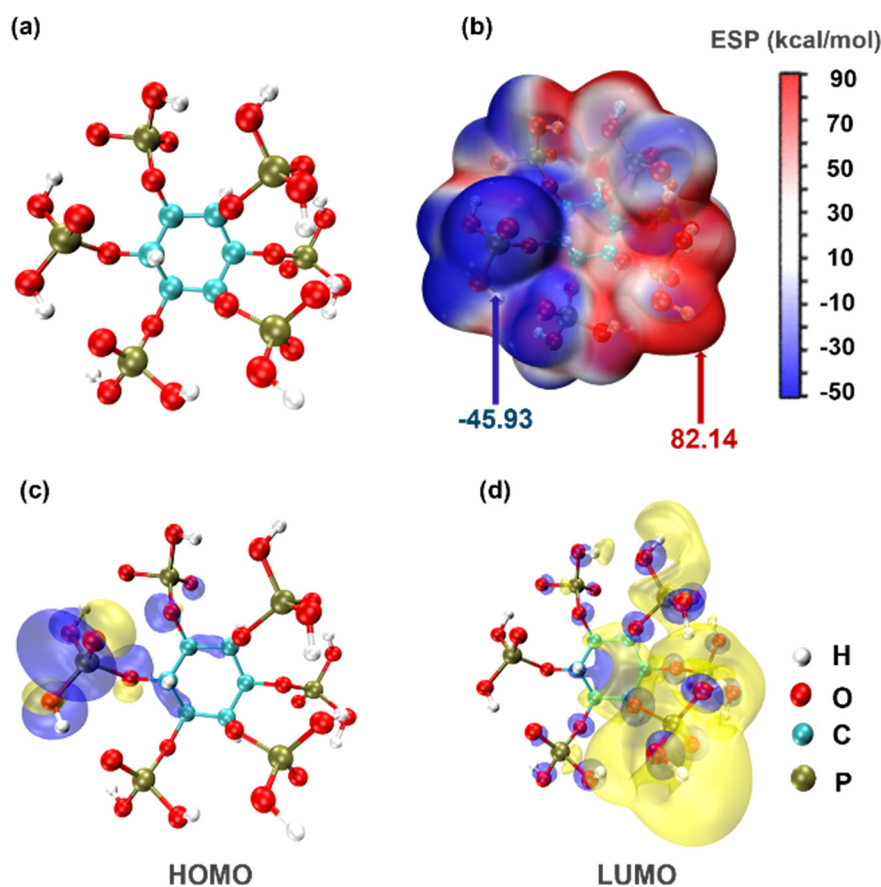


Figure 3. (a) Optimized structure, (b) electrostatic potential map, (c) HOMO orbital diagram, and (d) LUMO orbital diagram of the PA molecule.

The frontier molecular orbitals—HOMO and LUMO—were analyzed to understand PA's adsorption behavior on metal surfaces. Figure 3c,d show the HOMO and LUMO distributions, which correspond to the negative (blue) and positive (red) ESP regions, respectively. HOMO electron density is concentrated on oxygen atoms of two phosphate groups, enabling electron donation to metal unoccupied orbitals. LUMO density resides on the inositol ring and remaining phosphate groups, facilitating electron acceptance from metal filled orbitals. Generally, higher E_{HOMO} favors electron donation, while lower E_{LUMO} favors electron acceptance. Table 2 lists E_{HOMO} , E_{LUMO} , and related quantum chemical parameters, which can be compared with other inhibitors to predict inhibition performance. For instance, inhibitor molecules with a smaller ΔE value tend to adsorb more readily to form films, while higher electronegativity (χ) and lower hardness (η) indicate better inhibition efficiency.

Table 2. Global reaction parameters of PA molecules.

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (eV)	χ (eV)	η (eV)	S (eV)
PA	-7.567	-0.720	6.847	-4.143	4.143	3.423	0.292

Global parameters alone cannot pinpoint specific reactive sites; thus, Fukui function analysis was conducted to identify PA's electrophilic and nucleophilic centers. Figure 4a,b reveal that the most favorable adsorption sites are located on oxygen and hydrogen atoms. The Fukui index quantifies atomic electron donation/acceptance: higher f^- values indi-

cate stronger electron-donating ability, while higher f^+ values indicate stronger electron-accepting ability. Table 3 lists atoms with prominent Fukui indices. The results show that O22, O31, and O34 are electrophilic centers prone to losing electrons, whereas H43, H48, and P15 are nucleophilic centers with strong electron-accepting capabilities. These atoms exhibit high chemical reactivity and readily participate in electronic interactions with metals, promoting stable adsorption.

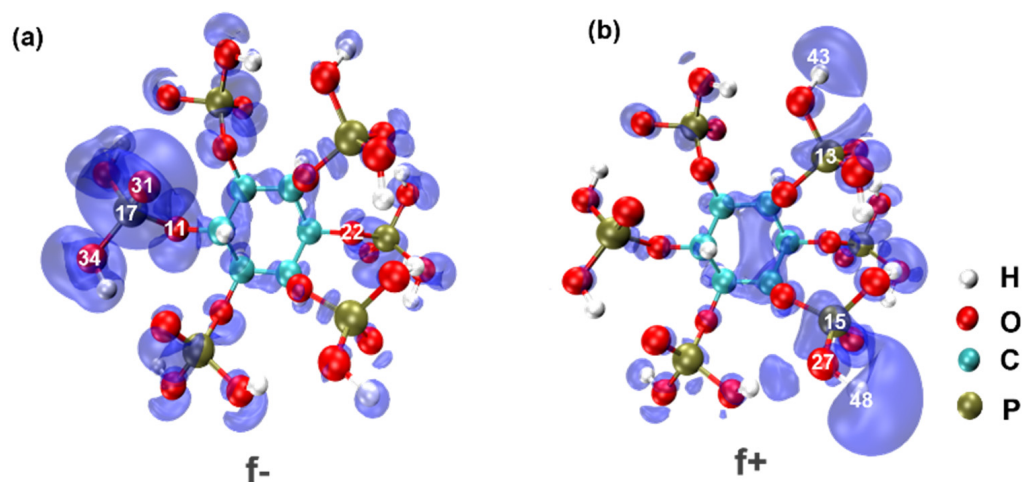


Figure 4. Fukui function for (a) electrophilic attack and (b) nucleophilic attack.

Table 3. Fukui indices of selected atoms in the PA molecule.

Molecule	PA				
$f^-(\vec{r})$	O11 0.0635	P17 0.0619	O22 0.0791	O31 0.1633	O34 0.0755
$f^+(\vec{r})$	P13 0.0387	P15 0.0495	O27 0.0435	H43 0.0505	H48 0.0795

3.2. Molecular Dynamics Simulations Results

3.2.1. Adsorption Configuration of PA Molecules on Metal Surfaces

Molecular dynamics simulations provide microscopic insights into molecular adsorption behavior on metal surfaces, elucidating the film formation mechanism. Figure 5 presents the adsorption configurations of PA molecules on Fe(110), Cu(111), and Al(111) surfaces in both PA aqueous solution and 3.5 wt% NaCl/PA mixed solution environments. PA molecules exhibit two primary adsorption configurations on metal surfaces: parallel adsorption and perpendicular adsorption relative to the metal surface. The adsorption configuration of PA molecules is determined by the chemical reactive sites within the molecule. Based on the analysis of the HOMO and LUMO orbital diagrams in Figure 3, the perpendicular adsorption configuration arises from interactions between the electron-donating phosphate groups of PA molecules and the metal surface, whereas the parallel adsorption configuration results from interactions between the electron-accepting moieties of PA molecules and the metal surface. As evident from Figure 5, the adsorption of PA molecules on metal surfaces effectively hinders the contact of water molecules and Cl^- ions with the metal surface, forming an adsorption film that can significantly mitigate metal corrosion.

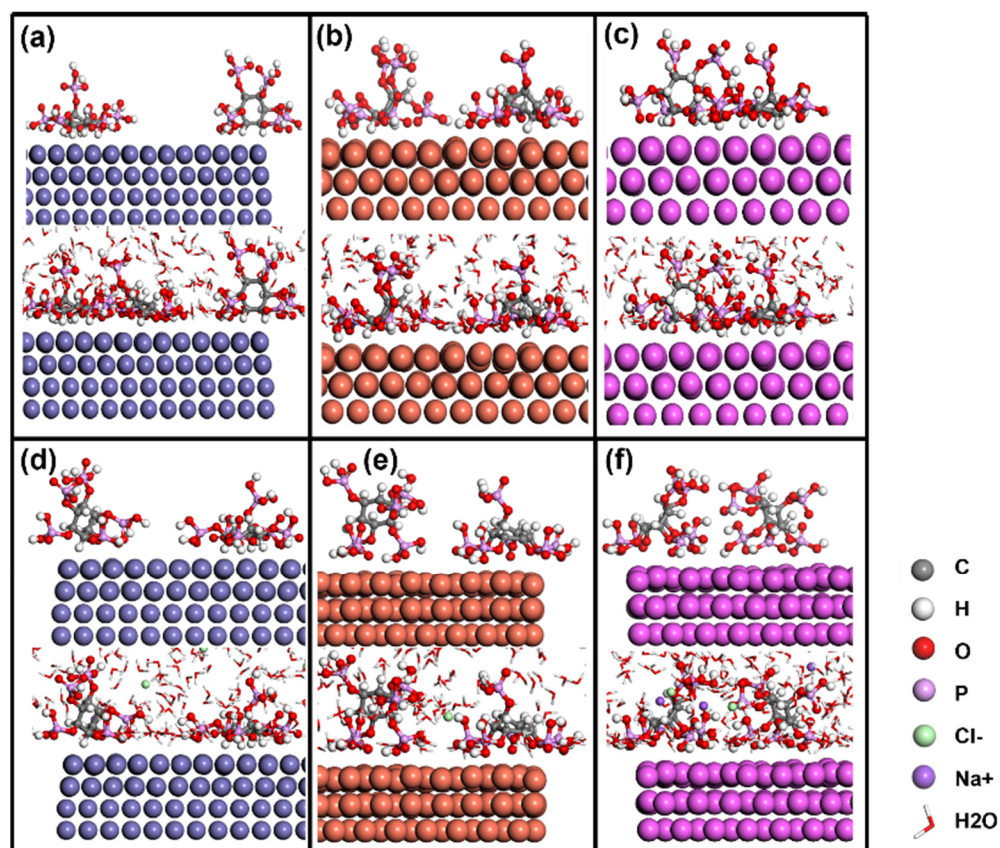


Figure 5. Adsorption configurations of PA on Fe, Cu, and Al surfaces: (a–c) in PA aqueous solution; (d–f) in 3.5 wt% NaCl/PA hybrid solution.

3.2.2. Adsorption Stability of PA Films

To investigate the stability of the adsorption films formed by PA molecules on the three metal surfaces, the adsorption energies of PA molecules on these surfaces in different solutions were calculated using the following formula:

$$E_{adsorption} = E_{total} - (E_{PA} + E_{surface}) \quad (8)$$

Here, $E_{adsorption}$ represents the adsorption energy of PA on the metal surface; E_{total} is the total energy of the combined PA–metal system; E_{PA} denotes the energy of the isolated PA molecule; and $E_{surface}$ is the energy of the bare metal surface. The obtained values are summarized in Table 4.

Table 4. Adsorption energies of PA on metallic surfaces in PA solution and NaCl/PA hybrid solution.

Metal Type	PA E_{ads} (kcal/mol)	NaClPA E_{ads} (kcal/mol)
Fe	−514.317	−504.516
Cu	−268.598	−232.502
Al	−235.568	−167.778

In the PA aqueous solution (denoted as PA in the table) and the NaCl/PA hybrid solution (denoted as NaClPA in the table), the adsorption energies of PA molecules on Fe, Cu, and Al metal surfaces are all negative, indicating that PA molecules can spontaneously adsorb onto the three metal surfaces, thereby preventing corrosive species from adhering to the metal surface. The adsorption stability of PA molecules on the substrate surfaces

can be evaluated by the absolute value of the adsorption energy: a larger absolute value corresponds to stronger adsorption of the molecule on the substrate and better corrosion protection effectiveness. In both solutions, the order of absolute adsorption energies of PA molecules on the three metal surfaces is consistently Fe > Cu > Al, demonstrating that the corrosion protection film formed by PA on the Fe surface exhibits the highest stability. Upon the addition of NaCl, the increased number of corrosive species in the PA/NaCl hybrid solution (NaClPA) leads to a decrease in the absolute values of the adsorption energies of PA molecules on the metal surfaces. Based on the absolute values of adsorption energies, the incorporation of NaCl has the least influence on the adsorption energy of PA on the Fe surface, a moderate effect on that of the Cu surface, and the most pronounced impact on that of the Al surface.

3.2.3. Distribution of Particles on Metal Surfaces

To further elucidate the interaction mechanism of PA molecules on metal surfaces, the radial distribution functions (RDF) of water molecules, PA molecules, and Cl^- ions on the metal surfaces were calculated in both PA solution and NaClPA solution environments, with the results presented in Figure 6. The radial distribution function characterizes the spatial distribution density of one type of particle around another within the structural environment, and its calculation formula is as follows:

$$g(r) = \frac{dN}{4\pi\rho^2} \quad (9)$$

where dN is the number of B particles located at a distance between r and $r + dr$ from particle A, and ρ is the average density of particle B.

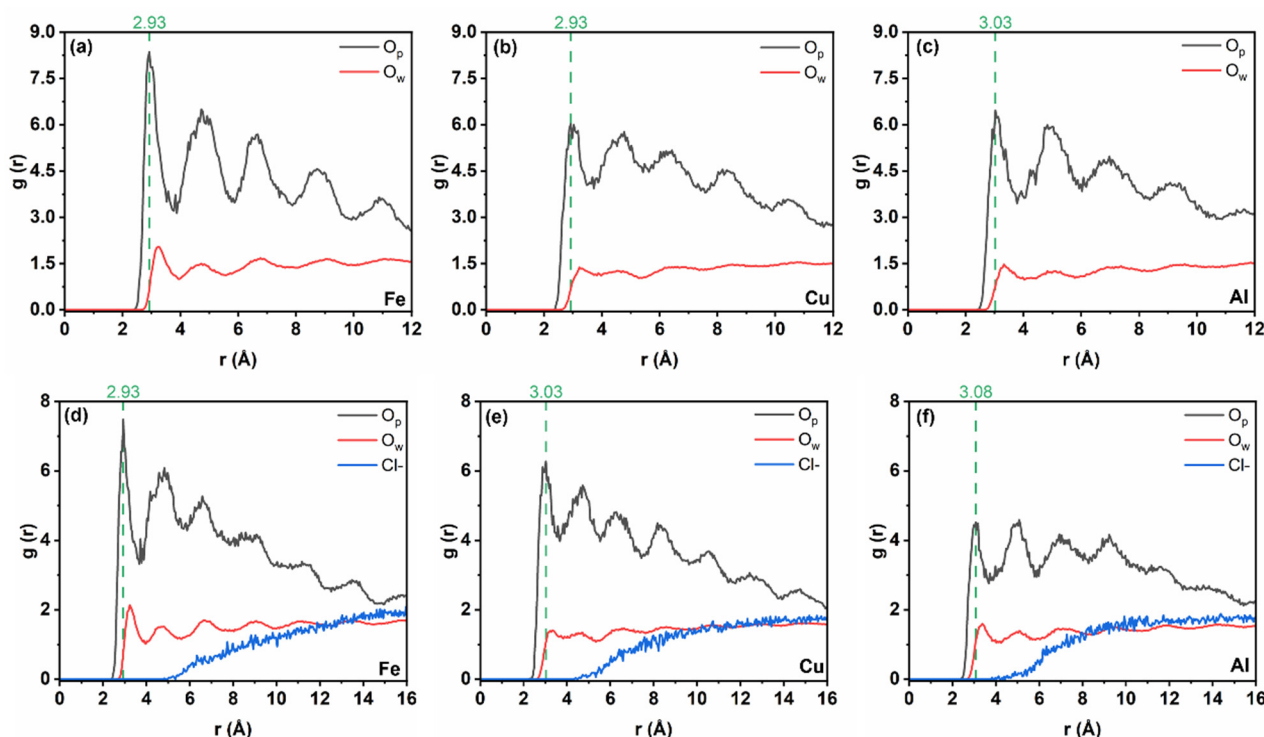


Figure 6. Radial distribution functions under different solution environments: (a–c) O_p (oxygen in PA) and O_w (oxygen in water) in PA solution; (d–f) O_p , O_w , and Cl^- in NaClPA solution.

PA molecules exhibit a distinct first sharp peak within the range of $r < 3.5$ Å on all three metal substrate surfaces. This indicates that PA molecules can form chemical bonds

with the three metal atoms. Consequently, PA molecules adsorb onto the metal surfaces via chemical bonding to form an adsorption film. This finding will be corroborated in the subsequent experimental section. The height of the RDF peak reflects the probability of occurrence at that specific distance. In both solution environments, PA molecules display the highest probability of occurrence on the Fe surface, demonstrating that PA molecules most readily adsorb onto the Fe surface, which is consistent with the calculated adsorption energies of PA molecules on metal surfaces. Due to the abundant hydroxyl groups present in PA molecules, hydrogen bonding interactions occur between water molecules and PA molecules, resulting in the appearance of peaks in the RDF curves of water molecules near the metal surface. In other regions of the solution, water molecules are uniformly distributed. The strong adsorption interaction between PA molecules and the metal surface causes Cl^- ions to begin appearing at positions farther from the metal surface, primarily distributed in the middle region of the solution layer, indicating that the adsorption of PA molecules effectively blocks corrosive species.

In aqueous environments, the presence of water molecules and Cl^- ions constitutes a significant factor contributing to metal corrosion. Therefore, obtaining dynamic information regarding the corrosion inhibition mechanism necessitates investigating the diffusion coefficients of water molecules and Cl^- ions. The diffusion coefficient serves as a quantitative indicator characterizing the diffusion capability of corrosive particles. In MD simulations, diffusion coefficients are calculated by fitting the mean square displacement (MSD) curves, with the calculation formula presented as follows:

$$\text{MSD} = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (10)$$

The particles in the system continuously move from their initial positions. Let $\vec{r}(0)$ denote the initial position of a particle and $\vec{r}(t)$ denote its position at time t , where the angle brackets $\langle \rangle$ represent the ensemble average. According to the Einstein diffusion equation, the diffusion coefficient of a given species can be calculated as:

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle}{6t} \quad (11)$$

That is, under equilibrium conditions, the diffusion coefficient is obtained by dividing the slope of the mean square displacement (MSD) curve by a factor of 6. The calculated diffusion coefficients are presented in Tables 5 and 6.

Table 5. Diffusion coefficients of water molecules in pure water solution and PA solution.

Substrate Type	Pure Water (H_2O) D ($\text{\AA}^2/\text{ps}$)	PA (H_2O) D ($\text{\AA}^2/\text{ps}$)
Fe	0.255	0.238
Cu	0.275	0.265
Al	0.285	0.254

Table 6. Diffusion coefficients of Cl^- in NaCl solution and NaClPA solution.

Substrate Type	NaCl (Cl^-) D ($\text{\AA}^2/\text{ps}$)	NaClPA (Cl^-) D ($\text{\AA}^2/\text{ps}$)
Fe	0.104	0.069
Cu	0.151	0.112
Al	0.178	0.043

Compared with the blank solution (PA-free solution), the introduction of PA molecules effectively reduced the diffusion coefficients of water molecules and Cl^- ions in the solution, thereby restricting their motion and making it more difficult for corrosive species to contact the metal surface. This phenomenon primarily arises from the steric hindrance effect and interfacial adsorption behavior induced by PA molecules as macromolecular additives. Previous studies [44] have confirmed that PA molecules, owing to their abundant hydroxyl groups, form hydrogen-bonding networks with water molecules. This not only increases the physical resistance to diffusion of H_2O and Cl^- in the solution but also consumes active sites on the metal surface through preferential interfacial adsorption of PA itself, thereby hindering the access of water molecules and Cl^- ions to the metal substrate and kinetically delaying both the initiation and propagation of corrosion.

To further elucidate the corrosion inhibition mechanism of PA molecules on the three metals, the relative concentration distributions of PA molecules, water molecules, and Cl^- ions along the (001) direction in both PA solution and NaClPA solution were calculated, with the resulting profiles presented in Figure 7. Owing to the approximate thickness of 16 Å for the metal surface layer in the model, the relative concentration of all species within this region is zero. PA molecules are predominantly distributed in the vicinity of the metal surface, with no PA distribution observed beyond approximately 25 Å in the adsorption model, indicating that PA molecules primarily adsorb onto the metal surface to form a protective film. Water molecules, due to their interactions with PA, exhibit a peak following the first PA peak, after which they become uniformly distributed throughout the remaining solution. Cl^- ions begin to appear at around 20 Å. Specifically, on Cu and Al surfaces, the maximum peak of the Cl^- relative concentration profile occurs at approximately 22 Å, whereas on the Fe surface, this maximum appears at around 29 Å. In all cases, these Cl^- peaks are located after the first peaks of both PA and water molecules, demonstrating that the adsorption of PA effectively blocks Cl^- ions.

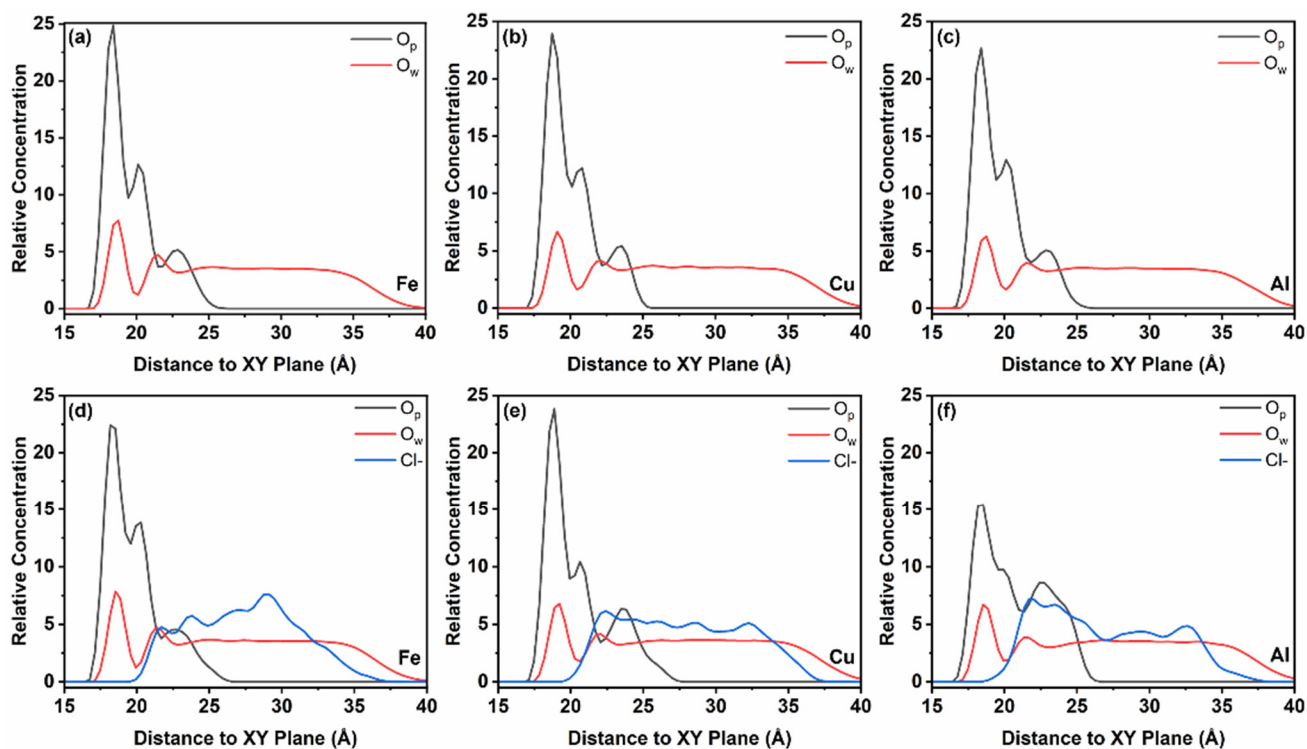


Figure 7. Relative concentration distributions under different solution environments: (a–c) O_p and O_w in PA solution; (d–f) O_p , O_w , and Cl^- ions in NaClPA mixed solution.

3.3. Compositional and Morphological Characterization of PA Conversion Films

The preceding quantum chemical calculations and molecular dynamics simulations have provided predictions at the atomic/molecular level regarding the adsorption behavior and inhibition mechanisms of PA molecules on Fe, Cu, and Al metal interfaces. The validity of these theoretical predictions, as well as the film-formation behavior under realistic conditions, requires macroscopic experimental validation.

To this end, PA conversion coatings were prepared on Fe, Cu, and Al metal surfaces via an immersion method. Their surface morphology and chemical composition were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

Figure 8 presents the morphological evolution and compositional changes of Fe, Cu, and Al surfaces before and after immersion in PA solution for 1 h, including corresponding SEM micrographs and EDS spectra of selected regions. Comparison of the SEM images before and after immersion reveals that a relatively uniform covering layer—identified as the PA conversion coating—is formed on all three metal surfaces following PA solution treatment. To ensure high-quality SEM observation and avoid sample charging effects, all specimens were sputtered with a thin gold (Au) layer prior to analysis.

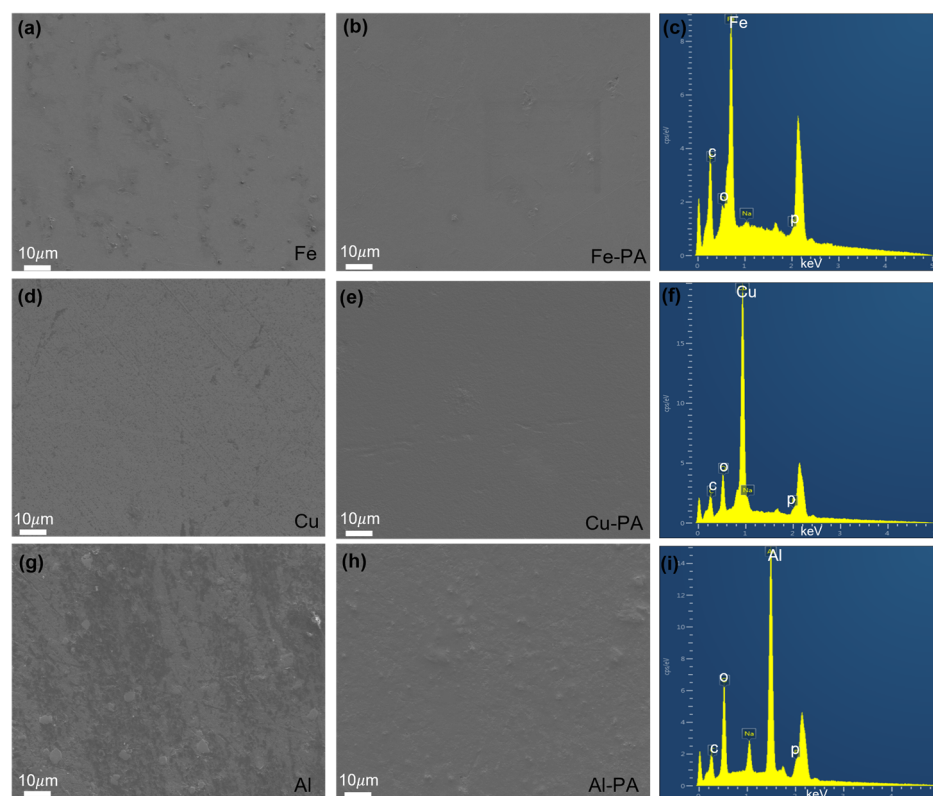


Figure 8. (a,d,g) SEM images of Fe, Cu, and Al metal surfaces before PA solution treatment; (b,e,h), SEM images of Fe, Cu, and Al metal surfaces after immersion in PA solution for 1 h; (c,f,i), corresponding EDS spectra.

The corresponding EDS compositional analysis reveals the presence of characteristic elements, including C, O, P, and Na, on all three metal surfaces after treatment. Notably, the prominent C, O, and P signal peaks directly correspond to the elemental constituents of PA molecules, confirming that the surface covering layer formed on the metals is indeed the intended PA conversion coating. Meanwhile, the detected Na signal originates from the NaOH reagent added during experimental preparation to adjust the pH of the PA solution, indicating residual Na⁺ ions present on the conversion coating surface or embedded within

the film structure. These results, which encompass both microstructural morphology and chemical composition, provide preliminary confirmation that phytic acid effectively forms conversion coatings on Fe, Cu, and Al surfaces.

To confirm the successful formation of PA conversion coatings from the perspective of chemical bonding, Fourier transform infrared spectroscopy (FTIR) was used to analyze the surfaces of Fe, Cu, and Al substrates before and after treatment with the PA solution. As shown in Figure 9, comparison of the FTIR spectra of the three metals before and after immersion reveals that significant characteristic absorption peaks appear exclusively on the Fe, Cu, and Al surfaces after PA solution immersion, located at approximately 1135 cm^{-1} , 1045 cm^{-1} , 1140 cm^{-1} , and 1650 cm^{-1} . These peaks can be definitively assigned to the stretching vibration of P=O bonds and the bending vibration of P–OH groups within PA molecules, respectively [28], indicating that PA interacts with different metal surfaces through the same active functional groups. This finding is consistent with literature reports [29,30,32] documenting the chelation and coordination bonding between phosphate groups and metal ions. These results not only confirm the formation of conversion coatings from a chemical composition perspective but also preliminarily elucidate the universal film formation mechanism, namely that PA establishes a stable surface protective layer primarily through specific chemical adsorption via its phosphate groups with the metals. The concurrent appearance of these characteristic functional group signals provides direct evidence that PA molecules undergo stable chemical interactions with each metal surface through their phosphate groups, rather than merely physical adsorption.

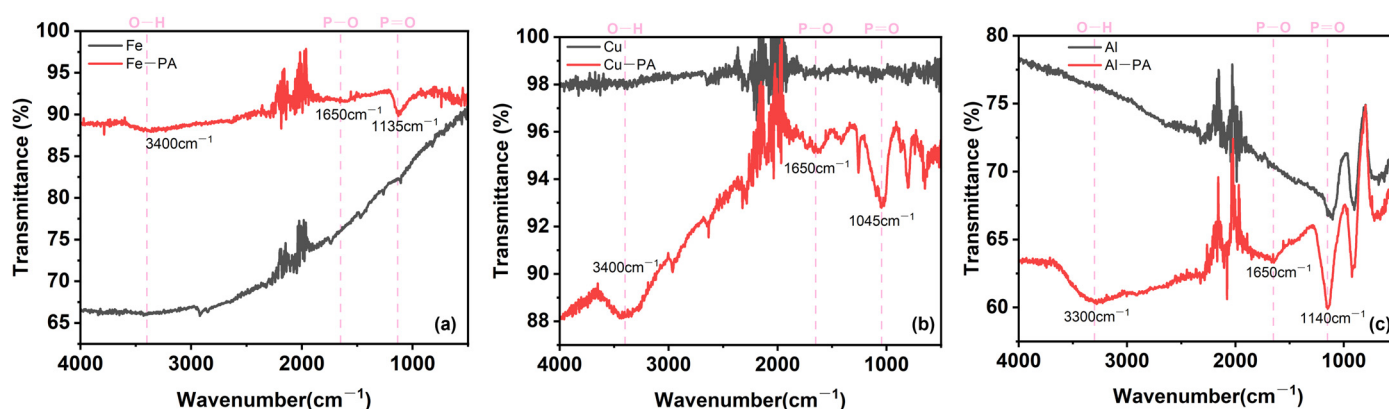


Figure 9. FTIR spectra of Fe, Cu, and Al metal surfaces before and after immersion in PA solution for 1 h.

3.4. Polarization Results

Figure 10 presents the polarization curves obtained for the three metals in 3.5 wt% NaCl solution before and after treatment with PA solution. Each polarization curve was analyzed using the Tafel extrapolation method to derive the corresponding corrosion current density (I_{corr}) and corrosion potential (E_{corr}). The inhibition efficiency (η) was calculated using the following formula [10,45]:

$$\eta = \left(\frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \right) \times 100\% \quad (12)$$

where I_{corr}^0 and I_{corr} represent the corrosion current densities of the metal surface in the absence and presence of the PA conversion coating, respectively. The calculated results are summarized in Table 7.

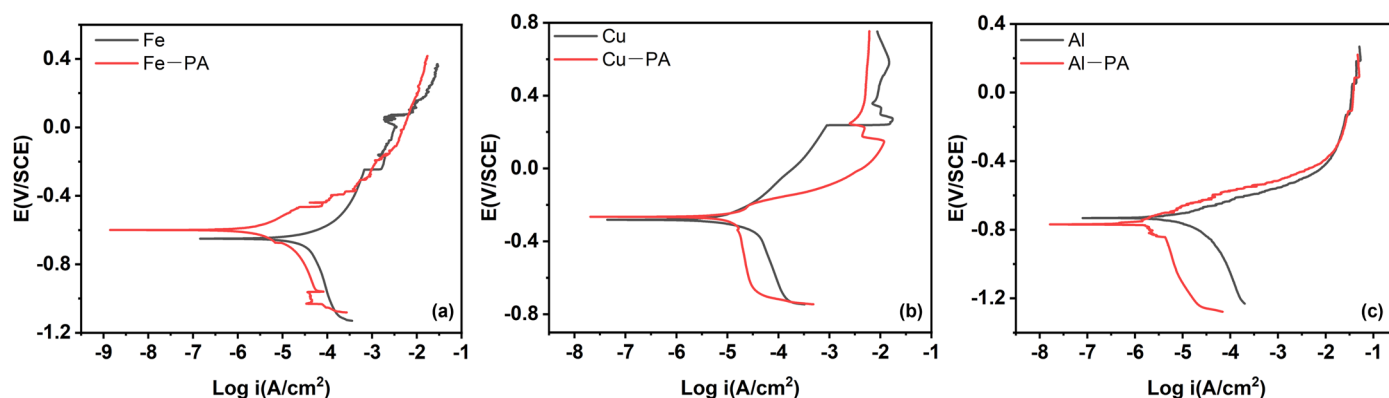


Figure 10. Polarization curves of Fe, Cu, and Al metals in 3.5 wt% NaCl solution before and after treatment with PA solution: (a) Fe, (b) Cu, (c) Al.

Table 7. Electrochemical fitting parameters derived from the polarization curves.

Samples	I_{corr} (A/cm ²)	E_{corr} (V/SCE)	η
Fe	2.72×10^{-5}	−0.66	---
Fe-PA	2.12×10^{-6}	−0.61	92
Cu	1.54×10^{-5}	−0.24	---
Cu-PA	1.14×10^{-5}	−0.22	26
Al	8.05×10^{-6}	−0.71	---
Al-PA	1.09×10^{-6}	−0.77	86.5

The polarization test results indicate that after treatment with PA solution, the corrosion current densities of Fe, Cu, and Al all decrease, demonstrating that the PA conversion coating provides universal corrosion inhibition. However, significant differences in inhibition efficiency (calculated from corrosion current densities) were observed among the different metals: Fe and Al achieved excellent inhibition efficiencies of 92% and 86.5%, respectively, while Cu exhibited a relatively low inhibition efficiency of only 26%.

In-depth analysis suggests that the limited protective performance on Cu primarily arises from the combined effect of its unique electrochemical characteristics and the constrained treatment time. The standard reduction potential of Cu^{2+}/Cu is +0.34 V vs. SHE, which is significantly higher than those of Fe^{2+}/Fe (−0.44 V vs. SHE) and Al^{3+}/Al (−1.66 V vs. SHE). This relatively high reduction potential makes direct oxidative dissolution of copper via hydrogen evolution difficult in H^{+} -containing environments; its corrosion process predominantly relies on oxygen-reduction cathodic reactions involving dissolved oxygen, resulting in a relatively slow anodic dissolution rate [29]. This sluggish dissolution kinetics limits the effective accumulation of copper ions (Cu^{2+}) at the metal/solution interface, thereby weakening the driving force for coordination deposition of PA molecules to form a conversion coating. Within the uniformly applied immersion time of 1 h in this experiment, compared to Fe and Al, which rapidly dissolve and provide high concentrations of $\text{Fe}^{2+}/\text{Al}^{3+}$ ions, the copper surface fails to develop a sufficiently thick, dense, and continuous PA conversion coating. This inadequacy compromises its barrier capability against corrosive species such as Cl^{-} and H_2O , ultimately manifesting as the observed lower corrosion inhibition efficiency.

4. Conclusions

This study systematically investigated the mechanism of PA on Fe, Cu, and Al metal surfaces by integrating quantum chemical calculations, molecular dynamics simulations, and experimental methods. The main conclusions are as follows:

- (1) Quantum chemical calculations identified the active sites of PA molecules, which, in combination with MD simulation results, revealed two adsorption configurations of PA on metal surfaces: perpendicular adsorption and parallel adsorption.
- (2) The negative adsorption energies of PA on all three metal surfaces indicate spontaneous and stable adsorption. The adsorbed PA film effectively inhibits the interfacial diffusion of corrosive species (H_2O and Cl^-) through steric hindrance, elucidating the physical barrier protection mechanism of the PA film at the atomic/molecular level.
- (3) PA conversion coatings were successfully fabricated on the three metal surfaces via a simple immersion method. Electrochemical tests confirmed that these coatings enhance the corrosion resistance of the metals. Under identical immersion conditions (1 h), the protection efficiency of the conversion coating on the Cu surface was relatively low, attributed to the slow oxidation process of Cu involving dissolved oxygen. Therefore, prolonged treatment time or the addition of oxidation promoters is recommended to facilitate PA conversion coating formation on Cu surfaces.

This work provides systematic theoretical and experimental support for the development of green and universally applicable surface treatment technologies based on natural products. It holds significant scientific importance and engineering application value for promoting environmentally friendly alternatives to traditional toxic passivation processes.

Based on the above findings, future work will focus on the following aspects:

- (1) Exploring process optimization strategies, such as extending the treatment time and introducing oxidation promoters for Cu-based materials, to improve the film quality and protection performance of PA conversion coatings.
- (2) Investigating the long-term protection performance of PA conversion coatings in other corrosive media (e.g., acidic and alkaline environments) and under complex service conditions to advance their engineering applications.

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