Sunflower Head Pectin with Different Molecular Weights as Promising Green Corrosion Inhibitors of Carbon Steel in Hydrochloric Acid Solution

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ABSTRACT: Three sunflower head pectin (SFHP) with different molecular weights ($M_w = 4.50, 97.23, $ and 254.64 kDa) were obtained by enzyme-assisted extraction and characterized by FTIR and $^1$H NMR spectroscopy. The corrosion inhibition of mild steel in 1 M HCl solution was evaluated by the weight loss measurement. The inhibition efficiency (IE%) increased as its concentration increases and decreased as the temperature increases. The SFHP with the lowest $M_w$ of 4.50 kDa exhibited an $I_{E_{\text{max}}}$ of 92.05% at the medium concentration (2.0 g L$^{-1}$). The inhibition properties of SFHP ($M_w = 4.50$ kDa) were investigated electrochemically and theoretically. The electrochemical impedance spectroscopy (EIS) revealed that the charge-transfer resistance increased as its concentration increases, the double-layer capacitance decreased as concentration increases, and the IE% also increased as concentration increases. The potentiodynamic polarization (PP) revealed that the double-layer capacitance decreased as concentration increases. The SFHP acted as mixed-type inhibitor. The IE% reached 90.3% at the medium concentration (2.0 g L$^{-1}$) of SFHP. The threedimensional super depth digital microscopy and scanning electron microscopy tests confirmed the formation of inhibitor films on the surface of mild steel. The adsorption of SFHP on the mild steel surface was proved to obey the Langmuir adsorption isotherm. The theoretical studies via density functional theory and molecular dynamics simulation further revealed the mechanism of corrosion inhibition.

1. INTRODUCTION

The use of inhibitors is recognized as one of the most economical and effective methods to defend metals against corrosion.$^{1,2}$ Many kinds of organic and inorganic compounds have been tested and applied as inhibitors to protect metals in industrial settings.$^{3,4}$ Despite their high performance, most of them are toxic, biorefractory, and expensive. During these years, in the context of environmental pollution, the choice of corrosion inhibitors should not only consider application efficiency issues but also, more importantly, environmental friendliness. In searching for highly efficient, readily available, relatively cheap, and eco-friendly inhibitors, numerous experimental studies have been undertaken on plant extractions and biomaterials as metal corrosion inhibitors in corrosive solution. Plant part extracts and organic components extracted from various plant parts acted as effective inhibitors,$^{5,6}$ such as pomegranate peel crude extract,$^7$ Ircinia strobilina crude extract,$^8$ sapota leaf extract,$^9$ and Lagerstroemia speciosa leaf extract.$^{10}$ However, corrosion researchers are committed to know the inhibitory active ingredients of plant extract inhibitors and performing separation and extraction. Organic sugars, flavonoids,$^{11}$ polyphenols, alkaloids,$^{12}$ and tannins can interact with a metal surface and obstruct corrosion active site. Most recent studies are therefore focused on the isolation of the active components responsible for the corrosion inhibition performance of plant extracts.

Pectin, a type of polysaccharide polymer, originates from natural plants. It is widely used in the food industry as a food additive.$^{13}$ Recently, because of its nontoxicity, biodegradability, and suitable molecular structure, it has attracted great interest as a corrosion inhibitor. Pectin extracted from citrus peel$^{14}$ was used to inhibit aluminum corrosion in HCl solution. The $I_{E_{\text{max}}}$ obtained at 10 °C using 8.0 g L$^{-1}$ concentration was about 91%, whereas it declined to 31% at 40 °C.$^{15}$ The citrus peel pectin also was used as a corrosion inhibitor for mild steel in 1 M HCl solution, and the $I_{E_{\text{max}}}$ obtained at 25 °C using 2.0 g L$^{-1}$ concentration was about 89%.$^{16}$ Pectin extracted from apple pomace acted as an inhibitor for X60 pipeline steel at 25 °C in 0.5 M HCl solution, and the $I_{E_{\text{max}}}$ reached 77% using 1.0 g L$^{-1}$ concentration.$^{17}$ Opuntia cladodes’ pectin exhibited an inhibition efficiency higher than 87% at the concentration between 0.125 and 1 g L$^{-1}$ at 25 °C.$^{18}$ The pectin was isolated from tomato peel waste and acted as a corrosion inhibitor for tin in 2% NaCl, 0.5% citric acid solution, and 1% acetic acid solution, and the $I_{E_{\text{max}}}$ obtained at 25 °C using 4.0 g L$^{-1}$ concentration was about 73%.$^{19}$ Using the same conditions, the $I_{E_{\text{max}}}$ of apple pectin for tin was 60% at the concentration of 4.0 g L$^{-1}$. These preliminary results have shown that pectin alone is a promising...
green corrosion inhibitor for metals in different corrosive media. The raw material resource, extraction conditions, and application conditions affected its inhibition performance. However, the relationship between the plant extraction structure and inhibition performance was not studied. The pectin corrosion inhibition properties should depend on its $M_w$ and degree of esterification (DE). Furthermore, the specific inhibition mechanism of pectin as a natural polymer was not proposed.

Thus, in this work, we focused on the SFHP, a low-ester pectin that was different from other pectin, and it was the first time using it as a corrosion inhibitor for carbon steel. The sunflower heads (a by-product of oil crop production) were selected as raw materials, and the pectin was obtained from sunflower heads by enzyme-assisted extraction, which achieved recycling of waste resources. Three SFHP with different molecular weights ($M_w$ = 4.50, 97.23, and 254.64 kDa) were first obtained by controlling different enzyme extraction conditions, and for the first time, they acted as corrosion inhibitors for mild steel in 1 M HCl solution. Three SFHP were characterized by FTIR and NMR spectroscopy. The corrosion inhibition performance of the three SFHP with different $M_w$ was studied by weight loss measurement, and the corrosion inhibition performance and the corrosion inhibition mechanism of the SFHP ($M_w$ = 4.50 kDa) with the best corrosion inhibition effect were studied by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), surface analysis, and theoretical studies.

2. RESULTS AND DISCUSSION

2.1. Characterization of SHFP. SHFP contains large amount of poly($\alpha$-galacturonic acid) bonded via $\alpha$-1,4-glycosidic linkage (Figure 1), and the structure was characterized by FTIR (Figure 2) and $^1$H NMR (Figure 3) spectroscopy.

FTIR spectra of SHFP are shown in Figure 2. A strong absorption, at about 3433 cm$^{-1}$, was due to the stretching vibration of hydroxyl groups. Formation of the inter and intramolecular hydrogen bonding of the galacturonic acid backbone might be the cause of this observation. Besides, the carbonyl bands, from 1706 to 1735 cm$^{-1}$ and 637 to 1607 cm$^{-1}$, represented the esterified and free carboxyl groups, respectively. The "finger print" region, between 1300 and 800 cm$^{-1}$, clearly demonstrated certain variations of pectin monosaccharide composition. The peaks in the region of 1010−1100 cm$^{-1}$ corresponded to the $\alpha$-glycoside bonds and $\beta$-glycoside bonds absorption. The DE was calculated as the peak area at 1713 cm$^{-1}$ (COOH$_3$) over the sum of the peak areas of 1641 cm$^{-1}$ (COOH) and 1713 cm$^{-1}$ (COOCH$_3$), and the obtained values of DE were 41.14, 40.24, and 30.14%.

The $^1$H NMR spectrum of SHFP is presented in Figure 3. Signals around $\delta$ 6.96, 3.68, 3.90, 4.34, and 5.08 were assigned to H-1, H-2, H-3, H-4, and H-5 of GaLa units. The signal of methyl group (−OCH$_3$) linked to the carboxyl groups (galacturonic acid) appeared at 3.68 ppm. The peaks at 2.10 and 1.96 ppm were due to acetyl groups with 2- and 3-O-galacturonic acid.

2.2. Weight Loss Measurements. Three samples with different $M_w$ values (154.65, 97.23, and 4.50 kDa) were tested as corrosion inhibitors for carbon steel in 1 M HCl solution, and the results are displayed in Figure 4 and Table 1. It could be observed that the IE$_w$% of the three SFHP samples increased with decreasing $M_w$ and the IE$_w$% of the three SHFP samples were ranked in the following order: 154.65 kDa $<$ 97.23 kDa $<$ 4.50 kDa. All of the IE$_w$% values for SFHP with $M_w$ = 154.64 kDa were lower than 50%, even displaying no anticorrosive activity at all at 25 and 30 °C. However, for SFHP with $M_w$ = 4.50 kDa, all the IE$_w$% values were higher than 50% at all tested temperatures. Such significant differences may be caused by the solubility of SFHP in the HCl solution. An effective inhibitor must have adequate solubility in the corrosive medium. Pectin molecules with higher $M_w$ were more entangled and therefore had lower solubility and IE$_w$% in HCl solution. On the other hand, SFHP with lower $M_w$ was more feasible, less entangled, and more uncoiled so better solubilities and IE$_w$% were obtained. Depending on the DE, the pectins were classified into low-methoxyl pectin (LMP, DE < 50%) and high-methoxyl pectin (HMP, DE > 50%). It was found that SFHP (DE = 40.24%) with $M_w$ = 97.23 kDa was a poor inhibitor in 1 M HCl solution, but citrus peel pectin (DE = 60%, $M_w$ = 30−100 kDa) was a good inhibitor. The original experiment by Fares et al. was conducted with aluminum. To eliminate the effect of the metal type, we performed corrosion experiments with C-steel using citrus peel pectin. The maximum IE$_w$% of 5.0 g L$^{-1}$ citrus peel pectin in 1 M HCl for C-steel at 15 °C was 87.65%. The results showed that citrus peel pectin (HMP) achieved a higher IE$_w$% than SFHP (LMP) of similar $M_w$. This may be related to the DE of the pectin. COOH functional groups in the pectin molecules were easily protonated into −COOH in highly acidic solutions. The repelling force among these positive charges stretches out the pectin molecule; hence, pectin molecules with higher $M_w$ became easily entangled. In the same $M_w$ range, LMP, which has more −COOH groups, was also more prone to entanglement and was less soluble than HMP. Therefore, reducing the molecular weight of LMP was an effective way to increase its solubility and IE$_w$%. However, lowering $M_w$ did not always increase IE$_w$%. Galacturonic acid, which was the basic unit of pectin, was also tested and found to be ineffective in inhibiting C-steel corrosion. This was likely

Figure 1. Molecular structure of SHFP.

Figure 2. FTIR spectra of SHFP.
because this molecule was too small to form a compact protective film. Hence, pectin as a high-performance corrosion inhibitor needs to be of an appropriate $M_w$.

Figure 4 shows that the pectin concentration and test temperature also had an effect on its $IE_{w\%}$. The $IE_{w\%}$ decreased with increasing temperature at constant concentrations. In acidic solutions, carbon steel corrosion was regularly accompanied by the production of hydrogen, which agitated the solution. The higher temperature accelerated the thermal motion of H$_2$ and inhibitors, causing the inhibitor molecules to easily detach from the carbon steel surface and increase the surface roughness. Hence, the $IE_{w\%}$ decreased with increasing temperature. $IE_{w\%}$ increased significantly with increasing concentration, especially in the lower concentration range (0.1–1.0 g L$^{-1}$). Inhibitors slowed metal corrosion by adsorbing onto the metal surface. At lower concentrations, all SFHP molecules in the solution were adsorbed onto the metal surface, leading to the approximately linear growth of $IE_{w\%}$ with the pectin concentration. At higher concentrations, however, adsorption saturation caused this correlation to become weaker since some pectin molecules were not utilized for inhibition.

2.3. Electrochemical Measurements of SFHP with $M_w = 4.50$ kDa. 2.3.1. Open Circuit Potential. It is necessary to ensure that there is a stable potential on the electrode surface before performing PDP and EIS tests. The OCP (vs SCE) versus time plots for the steel/blank solution interface at (25 ± 1) °C are shown in Figure 5. From Figure 5, the OCP value in the blank solution increased to nearly $-0.167$ V (vs SCE) after 600 s, which remained constant in the rest of the time. The corrosion inhibition system with different SHFP concentrations takes different times to obtain a stable OCP value, and the OCP value of the blank solution was lower than it. This phenomenon may be attributed to the SFHP that adsorb on the carbon steel surface and replaced chloride ions. The experimental results showed that a stable open-circuit potential can be obtained in 30 min, and then EIS and PDP tests were performed sequentially under this condition.

2.3.2. Potentiodynamic Polarization Curve. Due to its electrochemical inhomogeneity, the surface of carbon steel in HCl contained large numbers of microanodes and microcathodes, leading to short-circuiting of the microbattery reaction on the C-steel surface during corrosion. Hence, it was crucial to examine the anticorrosive activity of the inhibitor for both the anode and the cathode. Potentiodynamic polarization curves were used to obtain such information, and the test results are shown in Figure 6. Some of the polarization parameters obtained from these curves are listed in Table 2. The corresponding inhibition efficiency ($IE_p\%$) of SFHP can be calculated as$^{23}$
where \( I_{\text{corr}} \) and \( I_{\text{corr,0}} \) are the corrosion current densities of carbon steel with and without SFHP, respectively.

According to the polarization curves, an increased amount of SFHP reduced the current densities, and the reduction was more significant in the cathodic branch than in the anodic branch. Furthermore, the corrosion potential was notably moved in the cathodic direction as SFHP was added to the HCl solution, with the maximum shift of \( E_{\text{corr}} \) being +53 mV. These results suggested that SFHP acted as a mixed-type inhibitor with predominant control of the cathodic reaction. Organic corrosion inhibitors can be classified into three categories according to their modes of action, each with distinct corrosion potential changes as the inhibitor is added to the medium. No noticeable changes in \( E_{\text{corr}} \) and \( f_a/f_c = 1 \) were considered as signs of geometric blocking. The other two types, active site blocking and electrocatalytic inhibition, would cause obvious changes in \( E_{\text{corr}} \) and \( f_a/f_c \neq 1 \) (\( f_a < 1 \) and \( f_c < 1 \) in the former, \( f_a > 1 \) or \( f_c > 1 \) in the latter). The results in Table 1 showed that SFHP inhibited the corrosion of C-steel by active site blocking and that the SFHP molecules were preferentially adsorbed at cathodic active sites on the metal surface. This finding also confirmed that SFHP could effectively inhibit the corrosion of C-steel at \( E_{\text{corr}} \).

2.3.3. Electrochemical Impedance Spectroscopy. EIS was another valid means to explore the anticorrosive activity of inhibitors on the metal/solution interface. The test results are presented as Nyquist and Bode plots in Figure 7. A single capacitive loop implied that the corrosion process was
controlled by charge transfer. The Nyquist plots for the corrosion of carbon steel retained their original shape with the addition of the SHFP, revealing that the SHFP controlled the activity of the corrosion reaction instead of altering the corrosion mechanism. It can be seen that the corrosion rate decreased due to the presence of SHFP in the corrosion solution, as indicated by the increased diameter of the semicircle. The increased diameters of the semicircles indicated that the diffusion process was strongly blocked by the inhibitors.

From the Bode plots in Figure 7b, the peak heights increased with the concentration of the SHFP, which indicated that a protective film formed on the C-steel surface. The value of low-frequency impedance increased with the concentration increase.25 The change in microstructure at the interface of the metal solution might result in a shift of phase angle because a protective film would form onto the surface of the mild steel. Hence, with the increase in surface coverage, the phase shift would also increase. The SHFP formed a denser adsorption film on the surface of C-steel, which showed higher inhibition efficiency with the concentration increases.

Table 2. Polarization Parameters and the Corresponding Inhibition Efficiencies (IEp,%) for the Corrosion of C-Steel in 1 M HCl Solution Containing Different Concentrations of SFHP

| C (g L\(^{-1}\)) | \(E_{corr}\) (V SCE\(^{-1}\)) | \(I_{corr}\) (μA cm\(^{-2}\)) | \(f_e\) (V dec\(^{-1}\)) | \(f_e\) (V dec\(^{-1}\)) | \(f_e/f_c\) | \(R_p\) (Ω cm\(^2\)) | IEp (%) |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------|
| blank         | −0.203          | 1230            | −0.184          | 0.133           | −0.723          | 25.37           |         |
| 0.10          | −0.198          | 690             | −0.157          | 0.091           | −0.580          | 42.22           | 43.90   |
| 0.50          | −0.199          | 309             | −0.155          | 0.085           | −0.548          | 103.00          | 74.88   |
| 1.00          | −0.197          | 191             | −0.148          | 0.074           | −0.500          | 166.36          | 84.47   |
| 2.00          | −0.199          | 160             | −0.170          | 0.072           | −0.424          | 191.00          | 86.99   |
| 5.00          | −0.217          | 101             | −0.198          | 0.084           | −0.424          | 312.01          | 91.79   |

![Figure 7](image)

Figure 7. (a) Nyquist and (b) Bode plots of carbon steel in 1 M HCl solution with various concentrations of SFHP.

Corresponding equivalent circuits applied to analyze the impedance spectra are shown in Figure 8, and the fitted impedance parameters are listed in Table 3. Usually, the double-layer capacitance \(C_{dl}\) in the circuit would be replaced by a constant phase element (CPE) due to the frequency dispersion effect. The impedance of CPE was expressed as

\[
Z_{CPE} = \frac{1}{Q(j\omega)^n}\]

where \(Q\) is the CPE constant, \(j = \sqrt{-1}\), and \(\omega\) represents the angular frequency (rad s\(^{-1}\)) of the sine wave modulation. The index \(n\) is used to measure the surface inhomogeneity of the electrode. If \(n = 1\), the CPE is reduced to an ideal capacitor.26 The double-layer capacitance can be obtained as follows

\[
C_{dl} = (QR^{1-n})^{1/n}
\]

The corresponding inhibition efficiency, IEp%, is given by

\[
IE_p = \frac{(R_s + R_i + R_{ct}) - R_{std}}{R_s + R_i + R_{ct}} \times 100%
\]

where \((R_s + R_i + R_{ct})\) and \(R_{std}\) are the resistances of charge transfer with and without SHFP, respectively. According to Table 3, IEp% increased with \(C\), a trend already observed in the weight loss (I\(E_w\)% and Tafel polarization (IEp%) experiments.

Table 3 shows a series of electrochemical parameters, including film resistance \((R_f)\), film capacitance \((C_{dl})\), charge-transfer resistance \((R_{ct})\), double-layer capacitance \((C_{dl})\), solution resistance \((R_s)\), constant phase element (CPE), and inhibition efficiency (IEp%). \(R_s, R_{ct}\) and \(C_{dl}\) values were quite small compared with \(C_{dl}\) values, which illustrated that the corrosion process was mainly controlled by the electron transfer between the metal surface and the protective film. It can be seen that \(R_s\) increased with the increase in concentration, which confirmed that the SHFP adsorption film improved the corrosion resistance of C-steel. In addition, the decrease in \(C_{dl}\) was probably attributed to the replacement of the previously absorbed water.
molecules with large dielectric constants by the larger SHFP molecules with lower dielectric constants. As a result, the inhibition efficiency displayed an increasing trend with an increase in inhibitor concentration, and the value reached 92.88% at a concentration of 5.00 g L⁻¹.

2.4. Measurement of the Potential of Zero Charge. The thermodynamic parameters confirmed that the adsorption of SFHP onto the surface of C-steel was physical adsorption, which was related to the electrostatic attraction between the protonated SFHP and the charged carbon steel surface. The potential of zero charge (E_pzc) measurement was the most reliable method to estimate the charge on a metal surface. The corresponding results are shown in Figure 9. When the potential was −450 mV, the value of C_dl was at its minimum. This potential was assigned as the E_pzc of the C-steel in HCl solution with 5.0 g L⁻¹ SFHP (M_r = 4.50 kDa). Under the same conditions, the corrosion potential (−415 mV) was more positive than the E_pzc, indicating a positively charged metal surface in the corrosion-free environment.

2.5. Adsorption Isotherms and Thermodynamic Analysis. SFHP, which contains oxygen atoms and carboxyl groups, inhibits acid corrosion on the metal surface by forming a protective layer. This layer can be formed by one of the following adsorption mechanisms: (1) physisorption of SFHP on the steel surface due to the electrostatic attraction between the protonated carboxyl groups of pectin and the charged carbon steel surface; (2) chemisorption by forming coordinative bonds between the empty d orbital of Fe and the lone pair electrons of the O heteroatom; or (3) coexistence of the two adsorption modes above. Adsorption isotherms (Langmuir, Temkin, Freundlich, and Frumkin types) are often used to investigate the adsorption behavior and mechanism of inhibitors. Similar to other reported pectin, the Langmuir isotherm of SFHP fitted the data better than the other three kinds of isotherms mentioned above, with high regression coefficients (R²) ranging from 0.94−0.99. According to the Langmuir adsorption hypothesis, SFHP molecules adsorbed onto the C-steel surface by monolayer adsorption and without interacting with each other. The fitting plots are displayed in Figure 5. Changes in the standard free energy (ΔG_ads⁰), enthalpy (ΔH_ads⁰), and entropy (ΔS_ads⁰) of the adsorption process are important thermodynamic parameters, and they are calculated by the following equations:

\[ ΔG_{ads}^0 = -RT \ln(S) \]  
(5)

\[ \ln K_{ads} = - \frac{ΔH_{ads}^0}{T} + B \]  
(6)

\[ ΔG_{ads}^0 = ΔH_{ads}^0 - TΔS_{ads}^0 \]  
(7)

where K_ads is the adsorption equilibrium constant obtained from the intercept in Figure 10. ΔH_ads⁰ was obtained as the slope of the linear fit in the ln K_ads versus 1/T plot (Figure 11). R is the gas constant, T is the temperature, and B is a constant. All thermodynamic parameters are given in Table 4. Based on thermodynamic principles, ΔG_ads⁰ < 0, ΔH_ads⁰ < 0, and ΔS_ads⁰ > 0 indicating that the adsorption process was definitely spontaneous. Usually, an adsorption process was believed to be physisorption if |ΔG_ads⁰| < 20 kJ mol⁻¹ and chemisorption if |ΔG_ads⁰| > 40 kJ mol⁻¹. The values of |ΔG_ads⁰| in Table 4 were approximately 20 kJ mol⁻¹, indicating that the adsorption of SFHP on the C-steel surface occurs through physisorption. The values obtained for ΔH_ads⁰ led to the same conclusion. The
adsorption process was an exothermic reaction in which energy was released as pectin was spontaneously adsorbed onto the metal surface. Physical adsorption, due to its weak interaction force, was consistent with small $\Delta H_{\text{ads}}$ (i.e., $\Delta H_{\text{ads}}$ is rarely below $-40$ kJ mol$^{-1}$). In contrast, chemisorption normally released much more energy ($\Delta H_{\text{ads}} < -100$ kJ mol$^{-1}$) due to the much stronger chemical bonds. The value of $\Delta H_{\text{ads}}$ in Table 4 ($-6.23$ kJ mol$^{-1}$) also demonstrated that the SFHP adsorption here was physical adsorption. This corresponded to hypothesis (1) discussed in Section 2.5, and electrostatic attraction was the main force between pectin and the carbon steel surface.

2.6. Surface Analysis. 2.6.1. 3D Super Depth Digital Microscopy Analysis. Figure 12 shows digital microscopy photographs of carbon steel surfaces before and after exposure to 1 M HCl solution for 48 h at 25 °C, with and without 5.0 g L$^{-1}$ SFHP ($M_w = 4.50$ kDa). While the pristine C-steel surface (Figure 12a) had a smooth texture, which had an average depth of less than 11.04 μm after exposure to blank HCl solution (Figure 12b), many irregular erosion gullies developed on the surface, and the texture diminished due to corrosion by the acid solution, resulting in an average depth value of about 78.98 μm. In contrast, the surface of the sample immersed in HCl with pectin (Figure 12c) had only a few irregular shallow pits with an average depth value of about 20.64 μm, and the texture was clearly visible. A comparison of the surface morphology of these three coupons further confirmed that carbon steel corrosion in HCl solution was successfully inhibited by the added SFHP.

2.6.2. Contact Angle Measurement. The contact angles of the C-steel samples in the absence and presence of SHFP for 48 h immersion in 1 M HCl were investigated through water contact angle measurements, and the results are shown in Figure 13. The water contact angle of the polished C-steel samples surface was observed to be 80.60° ± 0.20, and it can be seen that the water contact angle decreased from 80.60° ± 0.20 to 47.25° ± 0.45 after immersion for 48 h. The decrease in contact angle was attributed to the increase in surface roughness caused by the corrosive attack of HCl. In comparison, the contact angle of C-steel samples (after 48 h immersion) in the presence of 5 g L$^{-1}$ SHFP increased to 70.55° ± 0.15, which suggested that the SHFP was continuously adsorbed and accumulated on the C-steel sample surface and provided a stronger protection ability for C-steel samples.

2.6.3. SEM-EDX Analysis. To analyze the C-steel surface morphology in 1 M HCl solution in the absence and presence of 5.0 g L$^{-1}$ SHFP ($M_w = 4.50$ kDa) after 48 h of immersion at 25 °C, it was tested by SEM-EDX. Analysis of the micrograph results was shown in Figure 14a–c. The surface of the C-steel was strongly corroded with remarkable localized pits (Figure 14b), which could be attributed to the corrosive attack by the 1 M HCl solution. Comparing Figure 14b with Figure 14a for polished C-steel, it was revealed that the C-steel surface exhibits uniform corrosion and is accompanied by localized corrosion. The C-steel surface, which in the presence of 0.5 g L$^{-1}$ SHFP is comparatively smoother than in its absence, further suggested that the SHFP molecules adsorbed on the surface of C-steel to form a protective film to prevent carbon steel corrosion. The N elements were detected on the C-steel surface (Figure 14c-1), and the intensities of C and O elements increased evidently, owing to the adsorption of SHFP molecules on the C-steel surface. Therefore, the EDX analysis also reveals that the SHFP molecules adsorbed on the C-steel surface to inhibit the dissolution of C-steel.

2.7. Computational Studies. 2.7.1. Quantum Chemical Study. The quantum chemical calculation was used to analyze the electron efficiency and molecular structure of SHFP monomers for corrosion inhibition. The optimized molecular structures and the frontier molecular orbital density distributions (LUMO and HOMO) of galacturonic acid in the aqueous phase were obtained from the B3LYP/6-311G** method, and the results are shown in Figure 15. The parameters obtained from the quantum chemical including $E_{\text{LUMO}}, E_{\text{HOMO}}, \mu$ (dipole moment), and $E_{\text{LUMO}} - E_{\text{HOMO}}$ are shown in Table 5. The frontier orbital energy parameters were calculated by eqs 8–10, which is according to Koopman’s theorem.

$$I = -E_{\text{HOMO}}$$  \hspace{1cm} (8)

$$A = -E_{\text{LUMO}}$$  \hspace{1cm} (9)

$$\Delta E_{\text{LUMO}} - E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$  \hspace{1cm} (10)

where $A$ represents the electron affinity of the molecule of SHFP, and $I$ represents the ionization potential.

The absolute electronegativity ($\chi$) was calculated by eq 11, which reflects the electron attraction ability of a group of atoms toward the SHFP molecule

$$\chi = \frac{1}{2}(I + A) = -\frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}})$$  \hspace{1cm} (11)

The global hardness ($\eta$) and the global softness ($\sigma$) can be calculated by eqs 17 and 18

$$\eta = \frac{1}{2}(I - A) = -\frac{1}{2}(E_{\text{HOMO}} - E_{\text{LUMO}})$$  \hspace{1cm} (12)

$$\sigma = \frac{1}{\eta}$$  \hspace{1cm} (13)
The fraction of electrons transferred between inhibitor molecules and the metal surface can be estimated according to the following equation

\[ \Delta N = \frac{x_{Fe} - x_{inhibitor}}{2(\eta_{Fe} + \eta_{inhibitor})} \]  

where \( x_{Fe} \) represents the absolute electronegativity of C-steel, \( x_{inhibitor} \) represents the absolute electronegativity of inhibitor, \( \eta_{Fe} \) represents the absolute hardness of iron, and \( \eta_{inhibitor} \) represents the absolute hardness of inhibitor. \( \Delta N \) reflects the electron donating ability and the trend of electron donation of the corrosion inhibitor molecule. To calculate the related parameters, we used a theoretical value \( x_{Fe} = 7 \) eV and a global hardness \( \eta_{Fe} = 0 \), assuming \( I = A \) for the bulk metal.34

The \( E_{\text{LUMO}}, E_{\text{HOMO}}, \) and \( \Delta E_{L-H} \) were directly related to inhibition efficiency. A higher value of \( E_{\text{HOMO}} \) means that the inhibitor has a higher inhibition efficiency and a stronger chemisorption ability. On the other hand, a lower value of \( E_{\text{LUMO}} \)...

Figure 12. Macromorphologies and 3D corrosion images of C-steel samples: (a) polished, (b) immersed in 1 M HCl without pectin, and (c) with 5.0 g L\(^{-1}\) SHFP.

Figure 13. Static water contact angle of C-steel samples: (a) polished, (b) immersed in 1 M HCl without pectin, and (c) with 5.0 g L\(^{-1}\) SHFP.
means that the inhibitor could accept electrons from the filled orbitals of metal via retrodonation, and the smaller energy gap means a greater inhibitor efficiency and a stronger chemisorbed bond. From Table 5, it was obvious that the galacturonic acid had a lower value of $\chi$, which suggested that the galacturonic acid has a higher tendency of electron donation. A higher value of global hardness ($\eta$) means the lesser tendency of electron transfer with the addition of galacturonic acid. However, the

Figure 14. SEM images of C-steel samples: (a) polished, (b) immersed in 1 M HCl without pectin, and (c) with 5.0 g L$^{-1}$ SHFP. (a-1)–(c-1) Corresponding EDS data of the red marked positions in (a–c).

Figure 15. Optimized molecular structures of galacturonic acid obtained from the B3LYP/6-311G$^{**}$ method and the frontier molecular orbital density distributions (LOMO and HOMO).
higher σ value means the higher reactivity of galacturonic acid. Thus, these data correlated well with those of the trend in the energy gap values shown above. From the data shown in Table 5, ΔN > 0 was for the galacturonic acid, so the electrons are transferred from the galacturonic acid molecule to the C-steel surface. Therefore, the trend of quantum chemical parameters obtained by calculation was consistent with the experimental results of corrosion inhibition efficiency. In summary, the inhibition capacity of SHFP could be ascribed to the adsorption of galacturonic acid constituents on the surface of the C-steel.

2.7.2. MD Simulation. MD simulations have been widely used in the discussion of the adsorption behavior of the inhibitor molecule on the metal surface so as to analyze the inhibition mechanisms in the atomistic level. We obtained the top and side views of the configurations of galacturonic acid over the Fe(110) surface, and the results are displayed in Figure 16. The information we obtained from Figure 16 was that the galacturonic acid molecules adsorbed on the Fe(110) surface with an almost flat orientation. It was beneficial for improving the surface coverage of galacturonic acid on the C-steel.

The parameters of $E_{\text{adsorption}}$ and $E_{\text{binding}}$ were used to analyze the extent of interaction of the galacturonic acid adsorbed on the Fe(110) surface, and they can be calculated by eqs 15 and 16

$$E_{\text{adsorption}} = E_{\text{total}} - (E_{\text{surface + solution}} + E_{\text{inhibition + solution}}) + E_{\text{solution}}$$

$$E_{\text{binding}} = -E_{\text{adsorption}}$$

where, $E_{\text{total}}$ is the total energy of the simulation system, $E_{\text{surface + solution}}$ is the total energy of the system without the inhibitor, $E_{\text{inhibition + solution}}$ is the total energy of the system without the iron crystal, and $E_{\text{solution}}$ is the total energy of the solution.

The calculated interaction energies and adsorption energies are listed in Table 6. It is obvious that it shows negative values of the binding energy between galacturonic acid and C-steel surface, which means that the interaction between galacturonic acid and C-steel carbon is stable and spontaneous.

3. MECHANISM OF CORROSION INHIBITION

Theoretical calculations and experiment results indicated that the SFHP with $M_w = 4.50$ kDa has a higher inhibition efficiency; it could be due to degradation of long pectin chains, through α-1,4-glycosidic linkage bond scission, to smaller but non-entangled segments. These smaller segments of SHFP could be adsorbed onto the surface of C-steel because they were easy to uncoil, thereby forming stable layers with protective effects to improve the inhibition efficiency. Therefore, reducing the molecular weight of LMP was an effective way to increase its solubility and IEw%. However, lowering $M_w$ did not always increase IEw%. Galacturonic acid, which was the basic unit of pectin, was also tested and found to be ineffective in inhibiting C-steel corrosion. This was likely because this molecule is too small to form a compact protective film. Hence, pectin as a high-performance corrosion inhibitor needs to be of an appropriate $M_w$.

The mechanism of corrosion inhibition of LMP is hereby proposed from the molecular level and schematically shown in Figure 17. $\text{Cl}^-$ was known to have a synergistic effect with inhibitors for corrosion inhibition. In this case, SFHP molecules were easily protonated in the acidic solution and were positively charged, making it difficult for them to adsorb onto the positively charged C-steel surface. Meanwhile, $\text{Cl}^-$ in the HCl solution can be adsorbed easily due to electrostatic interaction, making the net surface charge negative. $-\text{COOH}$ functional groups in the pectin molecules were easily protonated into $-\text{COOH}^2+$ in highly acidic solutions, which can form van der Waals bond with $\text{Cl}^-$ by electrostatic interaction. Eventually, the adsorbed SFHP molecules form a dense layer to protect the C-steel against corrosion. In summary, the electrostatic interaction between protonated SFHP and $\text{Cl}^-$ on the C-steel surface was the cause of the physical adsorption. The functional groups such as $\text{CH}_3\text{COO}^-$ and $-\text{O}^-$ in the SFHP molecular level could donate and share electrons to the empty orbital of iron, substituting aggressive substances on the steel surface and forming coordination bonds to adsorb on the metal surface.
thereby blocking the active sites exposed to corrosive media and reducing corrosion attack.

4. CONCLUSIONS

The following results can be drawn from this study:

(1) SFHP acted as efficient corrosion inhibitors of the carbon steel in 1 M HCl solution.

(2) The inhibition efficiency increased with increasing pectin concentration and decreased with increasing temperature.

(3) The low molecular weight could endow SFHP with good solubility, extra adsorption, and even higher corrosion inhibition efficiency.

(4) The corrosion process was inhibited by physisorption of SFHP on the carbon steel surface. Electrostatic attraction between the adsorbed Cl⁻ and protonated pectin molecules was the main driving force.

(5) SFHP were mixed-type inhibitors with predominant cathodic action, and the mode of inhibition was the blockage of active sites of corrosion.

(6) Experiments, DFT, and MD simulation were in good accordance with each other.

5. MATERIALS AND METHODS

5.1. Materials. Sunflower heads were collected from a farm in Shannxi Province of China in October 2018. d-galacturonic acid was purchased from Sinopharm Chemical Reagent Co. Ltd., cellulase enzyme (≥ 40 u/mg) was purchased from Shanghai Lanji Science and Technology Development Co., and citrus peel pectin (Mₘ = 30–100 kDa, DE = 60%) was purchased from Sigma. The reagents employed in this study were obtained from the following commercial sources: cellulase enzyme (AR, Aladdin Reagents (Shanghai) Co., Ltd.), citric acid (AR, Aladdin Reagents (Shanghai) Co., Ltd.), and sodium citrate (AR, Aladdin Reagents (Shanghai) Co., Ltd.). The components of the carbon steel (C-steel) used in all corrosion experiments were as follows: 0.5% C, 0.37% Si, 0.8% Mn, 0.04% P, 0.045% S, 0.25% Cr, 0.25% Ni, 0.25% Cu, and 97.495% Fe. The dimensions of the C-steel coupons used for weight loss and electrochemical measurements were 25.0 mm × 10.0 mm × 2.0 mm, respectively.

5.2. Extraction of Sunflower Head Pectin Samples and Test Solutions. In pretreatment of sunflower heads, the sunflower heads were washed with deionized water to remove impurities. The samples were then divided into three portions and vacuum-dried at 60, 100, or 150 °C for 4 h. Finally, the three samples were separately crushed into powder in a grinder.

In extraction of pectin, 4.0 g of the prepared sunflower heads powder was added to a mixture of 100 mL of deionized water, 2.0 g of cellulase enzyme, 0.86 g of citric acid, and 1.74 g of sodium citrate. Pectin was extracted in a shaker at 60 °C for 4 h. Afterward, the mixture was boiled for 5 min to inactivate the cellulase and centrifuged at 6000 rpm for 20 min. In the subsequent step, the supernatant from centrifugation was filtered through G3 sintered discs to remove solid residues, and the supernatant was stored at 4 °C. Finally, 2.5× volume of 95% acidified ethanol was poured slowly into the cooled supernatant, followed by filtration through cheesecloth. Pectin (the white floc) was rinsed with 95% ethanol and vacuum-dried. The dried pectin was ground and stored for follow-up tests. The DE value of SFHP was measured using the titrimetric method. The Mₘ was determined by a method modified from that reported by Zhang et al. A sodium nitrate solution (50 mM) containing 0.02% sodium azide (NaN₃) was used as the mobile phase at 35 °C. Dextran standards (Mₘ = 180, 3650, 20,100, 62,600, 102,000, and 226,700 Da; Sigma) were used to establish the standard curve (logMₘ = −0.5059x + 11.472; R² = 0.992). The Mₘ and DE values of SFHP extracted at 60, 100, and 150 °C are 154.64 kDa and 41.14%, 97.23 kDa and 40.24%, and 4.50 kDa and 30.14%, respectively. The SFHP with different Mₘ were characterized by FTIR and ¹H NMR spectroscopy, and the results are given in Section 2.1.

The test solutions used in corrosion experiments (1 M HCl with or without SFHP) were prepared according to the following process. A given amount of pectin sample (0.1, 0.5, 1.0, 2.0, or 5.0 g L⁻¹) was dissolved in 250 mL of deionized water and transferred to a 500 mL volumetric flask. Concentrated 37% HCl and deionized water were used to adjust the HCl concentration and volume of the solution to 1 M and 500 mL, respectively.

5.3. Weight Loss Measurements. The strip C-steel coupons (50 by 25 by 2) were prepared as the static weight loss test specimens, abraded with a series of emery papers (grades 400, 800, 1500, 3000, 5000, and 7000), and washed with distilled water and acetone in sequence. After washing, the cleaned samples were dried in warm air flow and weighed accurately with a sensitivity of ±10⁻⁴ g. Then, the samples were immersed in 500 mL of 1 M HCl solution with and without various concentrations of SHFP at given temperatures (15, 20, 25, and 30 °C). After 48 h immersion, the samples were taken out, washed again with distilled water and ethanol, and finally dried to constant weight. In the present study, each test solution containing three coupons was carried at ambient conditions, and the average values of three replicates are reported.

The corrosion rate (R_c) was calculated according eq 17, and the inhibition efficiency (IEₚ, %) was calculated according to eq 18.

\[
R_c = \frac{M_0 - M}{At}
\]

\[
IE_p, \% = \frac{R_{CO} - R_{CI}}{R_{CO}} \times 100\%
\]

where \(M_0\) and \(M\) are the weights (mg) of the C-steel before and after immersion in HCl solution, respectively. \(A\) (cm²) is the surface area of the test coupon, and \(t\) is the test time. \(R_{CO}\) and \(R_{CI}\) are the corrosion rates of C-steel coupon in 1 M HCl without and with SFHP, respectively.

5.4. Electrochemical Impedance and Potentiodynamic Polarization Curves. Electrochemical measurements were carried out on an electrochemical workstation (IM6, Zahner, Germany) using a three-electrode system at 25 °C (± 1 °C) in the prepared inhibited solutions. The three-electrode system included a saturated calomel electrode (reference electrode), a platinum sheet (counterelectrode), and a C-steel coupon enwrapped in epoxy resin with only one exposed surface of 1.0 cm × 1.0 cm (working electrode). To obtain a stable open-circuit potential (E_open) and ensure that the SHFP molecules were adsorbed on the C-steel surface, the electrodes need to be immersed in the test solution for 30 min. The electrochemical impedance spectroscopy (EIS) was performed by sweeping from 15 kHz to 10 mHz at E_open with an amplitude of sinusoidal disturbance of 10 mV. We used the Zsimpwin 3.10 impedance analysis software to fit the impedance curves, and we obtained the equivalent circuits and relevant parameters.
Finally, the polarization curves were obtained by sweeping from −0.8 to 0.5 mV at 1 mV/s scan rate.39 The polarization parameters, which include corrosion current density, corrosion potential, and Tafel slope, were obtained by Tafel extrapolation.

5.5. Measurement of the Potential of Zero Charge. EIS was performed in the test solution with 5.0 g L⁻¹ SFHP at different potentials. The double-layer capacitance (Cdl) at each potential was calculated from the obtained data and plotted on a curve versus the potential (V). The potential of zero charge (Epzc) was then determined as the applied potential where Cdl was at the minimum in the curve.

5.6. Surface Analysis. 5.6.1. 3D Super Depth Digital Microscopy Analysis. The surface morphology of C-steel in pristine condition and after corrosion in HCl solution without and with 5.0 g L⁻¹ SFHP was investigated using a digital microscope (VHX-2000, Keyence, Japan). The surface morphology and 3D corrosion depth maps were obtained at a magnification of 500X.

5.6.2. Contact Angle Measurement. The characteristic hydrophilic or hydrophobic behavior of 5.0 g L⁻¹ SFHP in 1 M HCl solution was investigated directly by the water contact angle measurement. Water (10 μL) was dropped onto the medium steel surface using a microsyringe, and the average of contact angles was reported by taking the measurement from similar images taken along the interface of carbon steel and water droplet at several locations. The steel surfaces were analyzed after 48 h immersion in 1 M HCl. All the measured contact angles are shown in Figure 13.

5.6.3. Scanning Electron Microscopy Analysis (SEM). The surface morphologies of the C-steel samples were observed by scanning electron microscopy (SEM) using Hitachi S-4800. The surface morphology and 3D corrosion depth maps were obtained at a magnification of 500X.

5.7. Computational Studies. The galacturonic acid residue was the structural unit of the main chain of the pectin molecule. Therefore, the adsorption of pectin molecules was simulated by using galacturonic acid to study the inhibition mechanism of pectin.

5.7.1. Quantum Chemical Studies. The quantum chemical calculations used the Gaussian-03 software package, and we obtained the geometrically optimized configuration of galacturonic acid at the B3LYP level of DFT using the 6-311G* (d, p) basis set for all atoms. The key parameters of quantum chemical calculations including the lowest unoccupied molecular orbital ($E_{LUMO}$), highest occupied molecular ($E_{HOMO}$), energy gap ($\Delta E$), global softness ($\sigma$), global hardness ($\eta$), number of transferred electron ($\Delta N$), and the absolute electronegativity ($\chi$) of galacturonic acid were obtained.

5.7.2. Molecular Dynamics (MD) Simulation. MD simulation studies used the software of Material Studio 5.5. The Fe(110) plane, which is the most densely and stably packed, was chosen to model a simulation box (2.86 nm × 4.05 nm × 5.89 nm) with periodic boundary conditions. Therefore, Fe(110) was first cleaved from the pure Fe crystal and then converted to an appropriate super cell by putting a vacuum space with a thickness of about 3 nm. The triazine derivative molecule with energy-minimized geometry was added to this super cell and positioned above its atomic row. The MD simulation was carried out in a water condition, and the adsorption system constructed by the Amorphous Cell Program included 982 H2O, 18 H3O⁺, 18 Cl⁻, and 1 galacturonic acid molecule. The corrosion system was built via placing the Amorphous Cell on the Fe(110) super cell by Layer Builder, and the super cell was kept fixed. The MD simulations were performed by the COMPASS force field under NVT ensemble at 298 K with a time step of 0.1 fs and a simulation time of 500 ps.

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■ REFERENCES

(1) Putilova, I. N.; Balezin, S. A.; Barannik, V. P.; King, C. V. Metallographic Corrosion Inhibitors. J. Electrochem. Soc. 1961, 108, 234C.
(2) Harvey, T. J.; Walsh, F. C.; Nahlé, A. H. A review of inhibitors for the corrosion of transition metals in aqueous acids. J. Mol. Liq. 2018, 266, 160–175.
(3) Goyal, M.; Kumar, S.; Bahadur, I.; Verma, C.; Ebenso, E. E. Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review. J. Mol. Liq. 2018, 256, 565–573.
(4) Finsgar, M.; Jackson, J. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review. Corros. Sci. 2014, 86, 17–41.
(5) Anupama, K. K.; Ramya, K.; Shainy, K. M.; Joseph, A. Adsorption and electrochemical studies of Pimenta dioica leaf extracts as corrosion inhibitor for mild steel in hydrochloric acid. Mater. Chem. Phys. 2015, 167, 28–41.
(6) Chen, S.; Zhang, D. Study of corrosion behavior of copper in 3.5 wt.% NaCl solution containing extracellular polymeric substances of an aerotolerant sulphate-reducing bacteria. Corros. Sci. 2018, 136, 275–284.
(7) Ahmed, A. A.; Delphine, V.-R.; Emmanuel, R. Pomegranate peels crude extract as a corrosion inhibitor of mild steel in HCl medium: Passivation and hydrophobic effect. Mater. Corros. 2019, 14, DOI: 10.1007/s11094-019-11049-7.
(8) Fernandes, C. M.; Fagundes, T. D. F.; dos Santos, N. E. C.; Rocha, T. S. D.; Garrett, R.; Borges, R. M.; Muricy, G.; Valverde, A. L.; Ponzi; E. A. Irinca strobilina crude extract as corrosion inhibitor for mild steel in acid medium. Electrochim. Acta 2019, 312, 137–148.
(9) Lekbach, Y.; Li, Z.; Xu, D.; El Abed, S.; Dong, Y.; Liu, D.; Gu, T.; Koraichi, S. I.; Yang, K.; Wang, F. Salvia officinalis extract mitigates the microbiologically influenced corrosion of 304L stainless steel by Pseudomonas aeruginosa biofilm. Bioelectrochemistry 2019, 128, 193–203.
(10) Raghavendra, N.; Hüblikar, L. V.; Patil, S. M.; Ganiger, P. J.; Bhange, A. S. Efficiency of sapota leaf extract against aluminium corrosion in a 3 M sodium hydroxide hostile fluid atmosphere: a green and sustainable approach. Bull. Mater. Sci. 2019, 42, 226.
(11) Jokar, M.; Farahani, T. S.; Ramezanzadeh, B. Electrochemical and surface characterizations of morus alba pendula leaves extract (maple) as a green corrosion inhibitor for steel in 1 M HCl. J. Taiwan Inst. Chem. Eng. 2016, 63, 436–452.
(12) Raja, P. B.; Qureshi, A. K.; Rahim, A. A.; Awang, K.; Mukhtar, M. R.; Osman, H. Indole Alkaloids of Alstonia angustifolia var. latifolia as green inhibitor for mild steel corrosion in 1 M HCl media. J. Mater. Eng. Perform. 2013, 22, 1072–1078.
(13) Mollica, C.; Chiappo, F.; Conti, R. Extraction and characteriza-
tion of pectins from cocoa husks: A preliminary study. Food Chem. 2008, 107, 1353–1356.
(14) Nishikawa, H.; Liu, L.; Nakano, F.; Kawakita, F.; Kanamaru, H.; Nakatsuka, Y.; Okada, T.; Suzuki, H. Modified citrus pectin prevents...
(15) Fares, M. M.; Maayta, A. K.; Al-Qudah, M. M. Pectin as a promising green corrosion inhibitor of aluminium in hydrochloric acid solution. *Corros. Sci.* 2012, 60, 112–117.

(16) Fiori-Bimb, M. V.; Alvarez, P. E.; Vaca, H.; Gervasi, C. A. Corrosion inhibition of mild steel in HCL solution by pectin. *Corros. Sci.* 2015, 92, 19–26.

(17) Umoren, S. A.; Obof, I. B.; Madhankumar, A.; Gasem, Z. M. Performance evaluation of pectin as eco-friendly corrosion inhibitor for X60 pipeline steel in acid medium: Experimental and theoretical approaches. *Carbohydr. Polym.* 2015, 124, 280–291.

(18) Saidi, N.; Elmsellem, H.; Ramdani, M.; Chetouani, A.; Azazaoui, K.; Youssi, F.; Aouniti, A.; Hammouti, B. Using pectin extract as eco-friendly inhibitor for steel corrosion in 1M HCl media. *Drug Pharma Chemica* 2015, 7, 87–94.

(19) Grassino, A. N.; Halambek, J.; Djaković, S.; Brnčić, S. R.; Dent, M.; Grabarić, Z. Utilization of tomato peel waste from canning industry as a potential source for pectin production and application as tin corrosion inhibitor. *Food Hydrocolloids* 2016, 52, 265–274.

(20) Hosseini, S. S.; Khodaiyan, F.; Yarmand, M. S. Optimization of microwave assisted extraction of pectin from sour orange peel and its physicochemical properties. *Carbohydr. Polym.* 2016, 140, 59–65.

(21) Muñoz-Almagra, N.; Valadez-Carmona, L.; Mendiola, J. A.; Illáñez, E.; Villamiel, M. Structural characterization of pectin obtained from cacao pod husk. Comparison of conventional and subcritical water extraction. *Carbohydr. Polym.* 2019, 217, 69–78.

(22) Sastri, V. S. Green Corrosion Inhibitors: Theory and Practice; John Wiley & Sons: 2012, 10, 249.

(23) Singh, D. K.; Ebenso, E. E.; Singh, M. K.; Behera, D.; Udayabhanu, G.; John, R. P. Non-toxic Schiff bases as efficient corrosion inhibitors for mild steel in 1 M HCl: Electrochemical, AFM, FE-SEM and theoretical studies. *J. Mol. Liq.* 2018, 250, 88–99.

(24) Murum, M.; Saha, S. K.; Murmu, N. C.; Banerjee, P. Effect of stereochemical conformation into the corrosion inhibitive behaviour of double azomethine based Schiff bases on mild steel surface in 1 mol L⁻¹ HCl medium: An experimental, density functional theory and molecular dynamics simulation study. *Corros. Sci.* 2019, 146, 134–151.

(25) Behpour, M.; Ghoreishi, S. M.; Soltani, N.; Salavati-Niasari, M. The inhibitive effect of some bis-N, S-bidentate Schiff bases on corrosion behaviour of 304 stainless steel in hydrochloric acid solution. *Corr. Sci.* 2009, 51, 1073–1082.

(26) Toxqui-López, S.; Olivares-Pérez, A.; Marroquín-Ramírez, J.; Fuentes-Tapia, I. Effect of degree of hydrolysis of polyvinyl alcohol on the diffusion efficiency from the gratings recorded in polyvinyl alcohol with ferric chloride films. *Practical Holography XXXII: Displays, Materials, and Applications*; SPIE - International Society For Optics and Photonics: 2018, 1055811, DOI: 10.1117/12.2291050.

(27) Li, X.; Deng, S.; Xie, X.; Du, G. Synergistic inhibition effect of S-aminotetrazole and 4, 6-dihydroxypyrimidine on the corrosion of cold rolled steel in H₃PO₄ solution. *Mater. Chem. Phys.* 2016, 181, 33–46.

(28) Obof, I. B.; Madhankumar, A. Synergistic effect of iodide ion addition on the inhibition of mild steel corrosion in 1 M HCl by 3-amino-2-methylbenzylalcohol. *Mater. Chem. Phys.* 2016, 177, 266–275.

(29) Hu, Z.; Meng, Y.; Ma, X.; Zhu, H.; Li, J.; Li, C.; Cao, D. Experimental and theoretical studies of benzothiazole derivatives as corrosion inhibitors for carbon steel in 1 M HCl. *Corros. Sci.* 2016, 112, 563–575.

(30) Okafor, P. C.; Zheng, Y. Synergistic inhibition behaviour of methylbenzyl quaternary imidazole derivative and iodide ions on mild steel in H₃SO₄ solutions. *Corros. Sci.* 2009, 51, 850–859.

(31) Saleh, M. M.; Atia, A. A. Effects of structure of the ionic head of cationic surfactant on its inhibition of acid corrosion of mild steel. *J. Appl. Electrochem.* 2006, 36, 899–905.

(32) Lewis, D. F. V.; Ioannides, C.; Parke, D. V. Interaction of a series of nitriles with the alcohol-inducible isoform of P450: Computer analysis of structure—activity relationships. *Xenobiotica* 1994, 24, 401–408.