Corrosion Inhibition of Honeycomb Waste Extracts for 304 Stainless Steel in Sulfuric Acid Solution

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Abstract: The extract of honeycomb waste was studied as a corrosion inhibitor on 304 stainless steel in H$_2$SO$_4$ solutions. The honeycomb waste was obtained from beekeeping at Lawang-Malong, East Java, Indonesia. Electrochemical and scanning electron microscopy methods were used to investigate the performance of the corrosion inhibition process. The inhibition efficiency of the inhibitor (2000 mg/L) reached 97.29% in 0.5 M H$_2$SO$_4$ and decreased with the acid concentration. Kinetic parameters were calculated to explain the effect of acid concentration on the inhibition process. The study on the adsorption behavior of the extracts followed the Frumkin isotherm model. The adsorption of the inhibitor on the 304 stainless steel surface was confirmed by the negative and lower values of Gibbs free energy. The obtained scanning electron microscopy (SEM) images were confirmed by comparing the surface of the specimens with and without inhibitor after corroding for one week. The results indicated that the extract acted as a good inhibitor for 304 stainless steel in acid corrosion.

Keywords: inhibitor; honeycomb waste; 304 stainless steel; corrosion; electrochemical

1. Introduction

Honey industries generally extract honey by squeezing the honeycomb; at this point, the squeezed honeycomb is damaged and becomes an organic waste that has no market value. This honeycomb waste contains bees wax and honey sugars (i.e., fructose, glucose and sucrose). It has a refractive index of 1.4398–1.4451 at 75 °C, a melting point of 61–65 °C, an acid number of 17–22, an ester number of 70–90, and a saponification number of 87–102. Water and hydrocarbon content are less than 1% and lower than 14.5%, respectively [1]. However, the honeycomb waste still contains relatively high flavonoids since a small amount of the honey remains after the squeezing process [2]. It is reported that the organic flavonoids structures have an electronegative atom, conjugated double bonds or aromatic rings that can be exploited as a corrosion inhibitor [3–6]. Therefore, in this work, we evaluated the potential of honeycomb waste as a corrosion inhibitor for structural steel materials.

Because of its formability and corrosion resistance, 304 SS is one of the materials which is widely applied in industries [7–9]. The corrosion resistance property is due to the protective film of chromium oxyhydroxide [10]. However, particularly in acid solutions, 304 SS is very susceptible to corrosion due to the breakage of the passive film. The most effective and economical measure to overcome
this problem is the employment of an inhibitor [9,11–14]. In the present work, we investigated the performance of the honeycomb waste extract as a corrosion inhibitor in various concentrations of H$_2$SO$_4$ solution. The performance of the inhibitor was evaluated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) methods.

2. Materials and Methods

2.1. Materials

The experiments were conducted on 304 SS (0.04% C, 0.52% Si, 0.92% Mn, 0.030% P, 0.002% S, 9.58% Ni, 18.15% Cr and the balance Fe, in wt.). The dimension of the specimen was 4 cm × 1 cm × 1 mm. All parts of the specimen were covered by epoxy resin, except for 1 cm$^2$ on each end of the specimen. The uncovered part was abraded using emery paper with a grade of 500 and 2000 consecutively. Furthermore, they were washed thoroughly with demineralized water and acetone.

The acid solutions were prepared by diluting AR grade 98% H$_2$SO$_4$ (Merck, Darmstadt Germany). Honeycomb waste was obtained from Rimba Raya beekeeping at Lawang-Malang, East Java, Indonesia. Fifty grams of honeycomb powder was extracted by the maceration method using 50 mL of 99% ethanol (Merck). This mixture was shaken for 3 h then transferred into a separating funnel. The organic extract from bees wax propolis was obtained by evaporating the bees wax propolis waste.

2.2. Characterization of Honeycomb Waste Extract

The extract was characterized by Fourier-transform infrared spectroscopy (FT-IR; Shimadzu IR Prestige-21, Kyoto, Japan) using the KBr-disk technique. The extract was also analyzed using an ultra-high-performance liquid chromatography (UHPLC)-ACCELLA 1250 System (Thermo Scientific, Pasadena, CA, USA). The separation was performed using a Hypersil Gold analytical column, Pasadena, CA, USA (50 mm × 2.1 mm, 1.9 µm particle size) at 30 °C with a flowrate of 300 µL/min. Gradient elution was carried out with a binary system consisting of (A) 0.1% formic acid in bi-distilled water and (B) 0.1% formic acid in acetonitrile. The gradient elution setting was adjusted as follows: 0–0.6 min, 15% B; 2–4 min 100% B; 4 min 15% B; 6 min 20% B; 10 min 45%; 20 min 25% B. A 2 µL of sample was injected for analysis.

The tandem mass spectrometry (MS/MS) triple quadrupole mass spectrometer (TSQ QUANTUM ACCESS MAX from Thermo Finnigan, Stanford, UK) with an electrospray ionization source (ESI) operating in negative ionization mode equipped with TSQ Tune software (Stanford, UK) was used for compound identification. The operational conditions of ESI ionization were as follows: spray voltage, 3 kV; evaporation temperature, 250 °C; capillary temperature, 300 °C; pressure of sheath gas, 40 psi; and aux gas pressure, 10 psi. The relative amount of each compound in the extracts was also calculated. Identification of the compounds was conducted by evaluating the chromatogram and mass spectra with the standard library.

2.3. Electrochemical Measurement

Electrochemical experiments were carried out using three-electrode-cell system with platinum as the counter electrode (CE), Ag/AgCl (3 M KCl) as the reference electrode (RE) and the 304 SS specimen as the working electrode (WE). The test solution was prepared by dissolving 0, 1000, 2000, 3000 and 4000 mg/L inhibitor in each acid solution, that is, 0.5, 1.0, 1.5 and 2.0 M H$_2$SO$_4$ solution. All tests were carried at 25 °C.

The electrode was immersed in the test solution at open-circuit potential (OCP) to stable conditions before measurement. All experiments were carried out using Autolab PGSTAT128N (Herisau, Switzerland) equipped with Nova 1.11 software. The potentiodynamic polarization was measured at ±200 mV from $E_{corr}$ with a scan rate of 1 mV/s [15]. The Tafel plots obtained were extrapolated to get the corrosion parameters. Inhibition efficiency (IE %) was defined as:
\[ IE (%) = \frac{I_{\text{corr}} - I_{\text{corr(i)}}}{I_{\text{corr}}} \times 100 \] (1)

where \( I_{\text{corr}} \) and \( I_{\text{corr(i)}} \) represented the corrosion current density with and without inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) was performed at open-circuit potential (OCP) in the frequency range of 1000 to 0.1 Hz using the signal amplitude of 15 mA. \( IE\% \) from the EIS method was calculated using the following equation (Equation (2)):

\[ IE (%) = \frac{R_{\text{ct(i)}} - R_{\text{ct}}}{R_{\text{ct(i)}}} \times 100 \] (2)

where \( R_{\text{ct}} \) and \( R_{\text{ct(i)}} \) were the charge transfer resistance with and without inhibitor, respectively.

2.4. Surface Analysis

The specimens were immersed in 1.0 M, 1.5 M and 2.0 M H\(_2\)SO\(_4\) solution with and without inhibitor (2000 mg/L) for one week at ambient temperature. Then, the specimens were washed with demineralized water and dried at room temperature. The morphological structure of the 304 SS surface was observed using a scanning electron microscope (SEM; FEI Inspect S-50, Tokyo, Japan). Before observation, all specimens were sputtered with a 10 nm layer of gold.

3. Results

3.1. Characterization of Honeycomb Waste Extract

Figure 1 shows the characteristic of the flavonoid wavenumber. It includes a carbonyl group (C=O, ketone) at \( \lambda = 1712.67 \text{ cm}^{-1} \), O–H group at \( \lambda = 3367.48 \text{ cm}^{-1} \) and aromatic group (C=C–C=C) at \( \lambda = 1649.02; 1514.02; \text{ and } 1460.01 \text{ cm}^{-1} \).

![Figure 1. Fourier-Transform Infrared (FTIR) spectra of honeycomb waste extract.](image)

Chromatograph of the extract displays nine peaks, which indicates nine different compounds (Figure 2). A major compound is found at a retention time of 3.59 min (peak 3) with an area of 43.90%, which is identified as quercetin (Figure 3). Identification of the other peaks gives the following results: luteolin, 1; vitexin, 2; fisetin, 4; isohamnetin, 5; isoferulic, 6; apigenin, 7; pinobanksin, 8; and kaempferol, 9. The detailed analysis of these compounds is summarized in Table 1.
intermediates to determine the anodic dissolution of Fe by the following mechanism:

\[
\text{FeOH} + e^- + \text{FeOH} + M \leftrightarrow \text{FeM} + \text{OH}.
\]

The active sites of the main compound in the extract can interact with the vacant d orbital of Fe and form a thin protective layer [16,17]. The presence of an inhibitor gives two specific adsorbed intermediates to determine the anodic dissolution of Fe by the following mechanism:

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \leftrightarrow \text{FeH}_2\text{O}_{\text{ads}} \quad (3a) \\
\text{FeH}_2\text{O}_{\text{ads}} + \text{M} & \leftrightarrow \text{FeOH}^-_{\text{ads}} + \text{H}^+ + \text{M} \quad (3b) \\
\text{FeH}_2\text{O}_{\text{ads}} + \text{M} & \leftrightarrow \text{FeM}_{\text{ads}} + \text{H}_2\text{O} \quad (3c) \\
\text{FeOH}^-_{\text{ads}} & \rightarrow \text{FeOH}_{\text{ads}} + e^- \quad (3d) \\
\text{FeM}_{\text{ads}} & \leftrightarrow \text{FeM}^+_{\text{ads}} + e^- \quad (3e) \\
\text{FeOH}_{\text{ads}} + \text{FeM}^+_{\text{ads}} & \rightarrow \text{FeM}_{\text{ads}} + \text{FeOH}^+ \quad (3f)
\end{align*}
\]

Table 1. Identification of the honeycomb waste extracts using liquid chromatography-mass spectrometry (LC-MS).

| Peak | RT (min) | Area (uV s) | Height (uV) | Area (%) | Molecular Weight | Molecular Formula | Compound     |
|------|----------|-------------|-------------|----------|------------------|-------------------|--------------|
| 1    | 2.90     | 16,787.68   | 2813.08     | 1.17     | 286.24           | C_{15}H_{10}O_{6} | Luteolin     |
| 2    | 3.42     | 214,035.89  | 34,555.55   | 14.96    | 432.00           | C_{21}H_{20}O_{10}| Vitexin      |
| 3    | 3.59     | 628,240.32  | 95,418.53   | 43.90    | 301.90           | C_{15}H_{10}O_{7} | Quercetin    |
| 4    | 3.76     | 35,082.10   | 5569.59     | 2.45     | 287.00           | C_{15}H_{10}O_{6} | Fisetin      |
| 5    | 3.96     | 25,177.60   | 4213.24     | 1.76     | 315.00           | C_{16}H_{12}O_{7} | Isohamnetin  |
| 6    | 5.60     | 13,670.09   | 2334.22     | 0.96     | 194.00           | C_{10}H_{10}O_{4} | Isoferulic   |
| 7    | 17.50    | 39,787.95   | 4860.57     | 2.78     | 270.24           | C_{15}H_{10}O_{5} | Apigenin     |
| 8    | 19.1     | 241,347.00  | 29,633.18   | 16.87    | 272.00           | C_{15}H_{12}O_{5} | Pinobanksin  |
| 9    | 20.3     | 216,906.26  | 20,458.26   | 15.16    | 286.00           | C_{15}H_{10}O_{6} | Kaempferol   |

Figure 2. Chromatogram of honeycomb waste extract.

Figure 3. Molecule structure of quercetin.
\[
\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} \text{H}_2\text{O}
\]  

(3g)

where M represents the inhibitor species.

There are some active sites on the surface of corroded metal that are able to absorb activation energy. In this case, the inhibitors molecule can be adsorbed easily on the active sites of the surface with matched adsorption enthalpies. According to Equation (3a–g), water molecules on the metal surface are replaced to yield the adsorption of intermediate \( \text{FeM}_{\text{ads}} \) by inhibitor species (Equation (3e)). This reduces the amount of the species \( \text{FeOH}_{\text{ads}} \) which causes retardation of Fe anodic dissolution [16,18,19].

3.2. Potentiodynamic Polarization

The \( E_{\text{corr}} \) of 304 SS shifts to a higher potential with a similar pattern in all acid concentrations in comparison with the blank. The 2000 mg/L inhibitor gives the maximum shift difference (Figure 4) with the shift to the blank, which are 28.5 mV, 98.0 mV, 115.0 mV and 104 mV in 0.5 M, 1.0 M, 1.5 M and 2.0 M \( \text{H}_2\text{SO}_4 \) solutions, respectively. It confirms that the inhibitor acts as an anodic inhibitor in 1.0 M, 1.5 M and 2.0 M \( \text{H}_2\text{SO}_4 \) solutions (the displacement of the \( E_{\text{corr}} \) is more than 85.0 mV) but in 0.5 M the inhibitor acts as a mixed inhibitor [20]. This is also confirmed by the value of the anodic current density, which is lower than the cathodic.

![Tafel plots for 304 SS with and without inhibitor in 0.5 M (a), 1.0 M (b), 1.5 M (c), and 2.0 M \( \text{H}_2\text{SO}_4 \) solution (d).](image)

The maximum concentration that gives the highest number in IE\% is 2000 mg/L (Table 2). The corrosion rate of 304 SS decreases with an inhibitor of 1000–2000 mg/L and increases with a 3000–4000 mg/L inhibitor. It can be attributed to the adsorption behavior of the inhibitor on 304 SS/acid solution interface [9,21]. The increase of inhibitor concentration beyond 2000 mg/L leads to diminished corrosion protection. This may be caused by the withdrawal of inhibitor back into the bulk solution when the inhibitor concentration is close to or beyond the critical concentration. This leads to a weakening of the metal-inhibitor interactions and causes the replacement of the inhibitor with water or \( \text{SO}_4^{2-,} \), reducing its IE\% [21].
Table 2. Corrosion parameters for 304 SS in several H$_2$SO$_4$ concentrations with and without inhibitor.

| [H$_2$SO$_4$] (mg/L) | C$_{inh}$ | $\alpha$ (V/dec) | $\beta_c$ (V/dec) | $E_{corr}$ (V) | $I_{corr}$ (A/cm$^2$) | $C_R$ (mpy) | IE (%) |
|---------------------|----------|------------------|------------------|---------------|------------------------|-------------|--------|
| 0.5 M               | 0        | -7.958           | -0.286           | 2.19 x 10$^{-5}$ | 0.228                  | -           | -      |
|                     | 1000     | 0.224            | -0.794           | -0.033        | 2.67 x 10$^{-6}$      | 0.028       | 87.79  |
|                     | 2000     | 0.103            | 0.172            | -0.001        | 5.93 x 10$^{-7}$      | 0.006       | 97.29  |
|                     | 3000     | 0.062            | 0.359            | -0.278        | 7.97 x 10$^{-6}$      | 0.083       | 63.60  |
|                     | 4000     | 0.082            | -0.707           | -0.280        | 8.32 x 10$^{-6}$      | 0.087       | 61.99  |
| 1.0 M               | 0        | 0.073            | -0.422           | -0.382        | 8.83 x 10$^{-4}$      | 9.186       | -      |
|                     | 1000     | 0.056            | -0.111           | -0.346        | 2.03 x 10$^{-4}$      | 2.116       | 76.96  |
|                     | 2000     | 0.075            | 0.442            | -0.284        | 3.10 x 10$^{-5}$      | 0.323       | 96.49  |
|                     | 3000     | 0.072            | -0.138           | -0.354        | 3.38 x 10$^{-4}$      | 3.513       | 61.75  |
|                     | 4000     | 0.063            | -0.168           | -0.365        | 4.21 x 10$^{-4}$      | 4.376       | 52.36  |
| 1.5 M               | 0        | 0.101            | -0.238           | -0.372        | 1.62 x 10$^{-3}$      | 16.793      | -      |
|                     | 1000     | 0.074            | -0.119           | -0.335        | 2.94 x 10$^{-4}$      | 3.053       | 81.82  |
|                     | 2000     | 0.098            | -0.181           | -0.257        | 7.17 x 10$^{-5}$      | 0.745       | 95.56  |
|                     | 3000     | 0.053            | -0.103           | -0.362        | 6.55 x 10$^{-4}$      | 6.807       | 59.46  |
|                     | 4000     | 0.087            | -0.166           | -0.364        | 8.59 x 10$^{-4}$      | 8.929       | 46.82  |
| 2.0 M               | 0        | 0.165            | 0.360            | -0.403        | 3.97 x 10$^{-3}$      | 41.311      | -      |
|                     | 1000     | 0.066            | 0.069            | -0.359        | 6.26 x 10$^{-4}$      | 6.509       | 84.24  |
|                     | 2000     | 0.118            | -0.189           | -0.299        | 2.14 x 10$^{-4}$      | 2.227       | 94.61  |
|                     | 3000     | 0.068            | -0.345           | -0.376        | 2.15 x 10$^{-3}$      | 22.325      | 45.96  |
|                     | 4000     | 0.649            | 0.129            | -0.375        | 2.70 x 10$^{-3}$      | 28.086      | 32.01  |

3.3. Electrochemical Impedance Spectroscopy (EIS) Measurement

The performance of honeycomb waste extract as an inhibitor at corroding 304 SS in sulfuric acid was also studied by electrochemical impedance spectroscopy (EIS). Figure 5 shows the Nyquist plots of 304 SS with and without inhibitor. According to Figure 5, there is a semicircle at high frequencies and a straight line at low frequencies. High frequency semicircles are generally associated with the charge transfer at the electrode/electrolyte interface, such as an electrical double layer. A straight line at low frequencies indicate Warburg impedance (W) [22]. W attributed to the anodic diffusion process of oxygen transport from the bulk solution to the electrode surface [23].

Figure 6a,b are equivalent circuits used for the EIS spectra for 304 SS in both the absence and the presence of inhibitor, respectively. Figure 6a is the standard equivalent circuit with 4 parameters, that is, $R_s$, $R_{ct}$, CPE and W. $R_s$ represents the solution resistance, $R_{ct}$ is correlated with the charge transfer resistance of metal, CPE is the constant phase element and W is the Warburg impedance. A more complicated equivalent circuit occurred with the addition of the inhibitor (Figure 6b). According to Figure 6b, there are two parts of equivalent circuit when the first part ($R_s$, $R_{ct}$ and CPE) is the standard and the second part ($R_1$, $R_2$, $C_1$ and $C_2$) is the additional circuit. The first part indicates that the inhibitor attaches to the metal surface, which is shown by the increasing in the value of $R_{ct}$. The $R_{ct}$ increases along with the increased inhibitor concentration which is up to 2000 mg/L. A further increase of the concentration leads to a decrease in the value of $R_{ct}$ (Table 3). The $R_{ct}$ is inversely proportional to the corrosion rate and related to $\text{IE}\%$ [21,23]. The higher $R_{ct}$, the lower the 304 SS corrosion rate. Therefore, the inhibition process is more efficient. It is in line with the result of potentiodynamic polarization. Moreover, additional parameters appeared in the second part of the equivalent circuit that give more information about the effect of the inhibitor. These parameters are related to the formation of the other passive films on the metal surface [24]. It is probably due to the reaction between the inhibitor and the metal surface. The fitting results for electrochemical impedance spectroscopy (EIS) data for 304 SS in several H$_2$SO$_4$ concentration with and without inhibitor was summarized in Table 3.

The Bode plots consist of a one loop capacitive (Figure 7a–d). It indicates that the inhibitor is adsorbed on the 304 SS surface by the gradual replacement of water molecules and ions.
shows that increasing inhibitor concentration up to 2000 mg/L results in a more negative value of the phase angle. It showed that there is greater surface coverage and transfer charge resistance [25–27].

**Figure 5.** Nyquist plots for 304 SS with and without inhibitor in 0.5 M (a), 1.0 M (b), 1.5 M (c), and 2.0 M H₂SO₄ solution (d).

**Figure 6.** Equivalent circuit used to the EIS spectra for the absence (a) and the presence (b) of inhibitor in 304 SS corrosion at sulfuric acid solution.
Table 3. Fitting results of electrochemical impedance spectroscopy (EIS) data for 304 SS in several H₂SO₄ concentration with and without inhibitor.

| [H₂SO₄] (mg/L) | C_inh (mg/L) | R_0 (Ω cm²) | R_1 (Ω cm²) | CPE (F/cm²) | n | R_2 (kΩ cm²) | R_3 (kΩ cm²) | C_1 (F) | C_2 (F) | W | Y_W (Ω⁻¹ cm² s⁰) | χ² |
|----------------|--------------|--------------|--------------|-------------|---|-------------|-------------|---------|---------|----|----------------|-----|
| 0.5 M          |              |              |              |             |   |              |              |         |         |    |                |     |
| 0              | 7.307        | 27.961       | 8.30 × 10⁻⁴  | 0.8999      |   | –           | –           | –       | –       |    | 0.0839         | 0.0378 |
| 1000           | 7.584        | 252.100      | 9.91 × 10⁻⁵  | 1.0099      |   | –           | –           | 3.70 × 10⁻⁴ | 9.00 × 10⁻¹³ | 0.0032 | 0.2389 |
| 2000           | 2.797        | 389.97       | 1.80 × 10⁻⁴  | 0.8855      |   | –           | –           | 3.846   | 4.00 × 10⁻⁴ | 9.00 × 10⁻¹³ | 0.0026 | 0.1319 |
| 3000           | 5.406        | 350.37       | 1.40 × 10⁻⁴  | 0.9418      |   | –           | –           | 2.036   | 4.30 × 10⁻⁴ | 9.00 × 10⁻¹³ | 0.0029 | 0.1011 |
| 4000           | 4.511        | 315.58       | 1.40 × 10⁻⁴  | 0.9560      |   | –           | –           | 1.966   | 4.40 × 10⁻⁴ | 9.00 × 10⁻¹³ | 0.0032 | 0.1058 |
| 1.0 M          |              |              |              |             |   |              |              |         |         |    |                |     |
| 0              | 7.342        | 25.654       | 7.60 × 10⁻⁴  | 0.8674      |   | –           | –           | –       | –       |    | 0.0915         | 0.0163 |
| 1000           | 12.339       | 227.180      | 1.90 × 10⁻⁴  | 0.8939      |   | –           | –           | –       | –       |    | 0.0445         | 0.6122 |
| 2000           | –2.207       | 340.760      | 1.30 × 10⁻⁴  | 0.9109      |   | –           | –           | –       | –       |    | 0.0034         | 0.4138 |
| 3000           | –1.421       | 271.340      | 1.80 × 10⁻⁴  | 0.8847      |   | –           | –           | –       | –       |    | 0.0049         | 0.6476 |
| 4000           | 1.064        | 140.780      | 1.50 × 10⁻⁴  | 0.9336      |   | –           | –           | –       | –       |    | 0.0115         | 0.1446 |
| 1.5 M          |              |              |              |             |   |              |              |         |         |    |                |     |
| 0              | 2.779        | 25.607       | 5.30 × 10⁻⁴  | 0.862       |   | –           | –           | –       | –       |    | 0.1009         | 0.0279 |
| 1000           | –34.995      | 122.820      | 2.60 × 10⁻⁴  | 0.949       |   | –           | –           | –       | –       |    | 0.0113         | 0.3348 |
| 2000           | –2.944       | 342.560      | 2.60 × 10⁻⁴  | 0.895       |   | –           | –           | –       | –       |    | 0.0039         | 0.0438 |
| 3000           | –395.090     | 264.590      | 1.60 × 10⁻⁴  | 0.954       |   | –           | –           | –       | –       |    | 0.0044         | 0.7933 |
| 4000           | –85.645      | 257.450      | 2.30 × 10⁻⁴  | 0.915       |   | –           | –           | –       | –       |    | 0.0433         | 0.6357 |
| 2.0 M          |              |              |              |             |   |              |              |         |         |    |                |     |
| 0              | 0.865        | 15.330       | 0.87 × 10⁻²  | 0.866       |   | –           | –           | –       | –       |    | 0.2329         | 0.0513 |
| 1000           | 1.173        | 105.700      | 4.00 × 10⁻⁴  | 0.845       |   | –           | –           | –       | –       |    | 0.0284         | 0.0042 |
| 2000           | –1.762       | 276.930      | 1.90 × 10⁻³  | 0.895       |   | –           | –           | –       | –       |    | 0.0045         | 0.6122 |
| 3000           | –52.314      | 25.708       | 4.10 × 10⁻⁴  | 0.839       |   | –           | –           | –       | –       |    | 0.1715         | 0.0533 |
| 4000           | 3.809        | 17.723       | 1.15 × 10⁻³  | 0.777       |   | –           | –           | –       | –       |    | 0.1701         | 0.0279 |
The Bode plots consist of a one loop capacitive (Figure 7a−d). It indicates that the inhibitor is adsorbed on the 304 SS surface by the gradual replacement of water molecules and ions. Figure 7 shows that increasing inhibitor concentration up to 2000 mg/L results in a more negative value of the phase angle. It showed that there is greater surface coverage and transfer charge resistance [25–27].

**Figure 7.** Bode plots for 304 SS with and without inhibitor in 0.5 M (a), 1.0 M (b), 1.5 M (c), and 2.0 M H$_2$SO$_4$ solution (d). Bode modulus (left) and Bode phase (right).

### 3.4. The Effect of Acid Concentration

The relationship of the corrosion rate ($C_R$) against acid concentration ($C$) obeys the kinetic equation:

$$\ln C_R = \ln k + BC$$  \hspace{1cm} (4)
3.4. The Effect of Acid Concentration

The relationship of the corrosion rate of 304 SS (Figure 9a–d), Freundlich (Figure 9e–h), Temkin (Figure 9i–l) and Frumkin isotherms (Figure 9m–p). The best fit is shown by Langmuir (Figure 9a–d), Freundlich (Figure 9e–h), Temkin (Figure 9i–l) and Frumkin isotherms (Figure 9m–p). The increased k with inhibitor (Table 4) means that the extracts inhibit the corrosion process of 304 SS [28]. The decreased B with inhibitor (Table 4) indicates that the changes of the corrosion rate in inhibited acid are larger than in uninhibited acid [28].

Table 4. Calculation of the linear regression between lnCR and C for the 304 SS corrosion in H2SO4 solution.

| Systems  | R²   | k (mmpy) | B (M⁻¹) |
|----------|------|----------|---------|
| Blank    | 0.987| 1.944    | 1.503   |
| Inhibitor| 0.994| 0.045    | 1.931   |

3.5. Adsorption Isotherm and Thermodynamic Calculations

The corresponding plots of the adsorption isotherm are shown in Figure 9. These are the Langmuir (Figure 9a–d), Freundlich (Figure 9e–h), Temkin (Figure 9i–l) and Frumkin isotherms (Figure 9m–p). The best fit is shown by R²-square (Table 5), for this study follows the Frumkin isotherm (Equation (5)).

Frumkin equation:

\[
\log \left( \frac{\theta}{(1 - \theta)C} \right) = \log K_{ads} + a\theta
\]

where C is the inhibitor concentration, \( \theta \) is the surface coverage, \( K_{ads} \) is the adsorption equilibrium constant and \( a \) is an interaction parameter. The value of \( a \) indicates attraction or repulsion between adsorbed species for \( a > 0 \) and \( a < 0 \), respectively. When \( a = 0 \), it means no interaction and it becomes equivalent to the Langmuir isotherm [29]. The Frumkin isotherm considers lateral interactions between adsorbed inhibitor molecules indicating that the inhibitor displaces the water molecules from the 304 SS surface [30]. The interaction parameters were calculated from the slope of Figure 9m–p. The positive value of \( a \) (Table 6) indicates highly attractive lateral interactions in the adsorbed layer. The increase of the inhibitor concentration probably induces desorption of the inhibitor, which is already adsorbed at the 304 SS surface and then it dissolves into solution. It makes the interactions stronger between the inhibitor in the solution and leads to secondary desorption [29,30].
The positive value of physisorption \[13,31\]. The more negative value follows the order 0.5 M H₂SO₄ > 1.0 M H₂SO₄ > 1.5 M H₂SO₄ > 2.0 M H₂SO₄.

The thermodynamic parameters are summarized in Table 6. The negative and lower values of the heat of adsorption \(\Delta H_{\text{ads}}\) is related to the Gibbs free energy of adsorption \(\Delta G_{\text{ads}}\).

The negative value of \(\Delta S_{\text{ads}}\) confirms the exothermic nature of the metal dissolution process °.

\[
\Delta G_{\text{ads}} = -RT\ln(K_{\text{ads}})
\]

Where, \(K_{\text{ads}}\) is the adsorption equilibrium constant.

The thermodynamic parameters are summarized in Table 6.

Table 5. R–Square of various isotherm for the adsorption of the inhibitor on 304 SS surface in 0.5 M, 1.0 M, 1.5 M and 2.0 M H₂SO₄, respectively.

| Systems       | Isotherm | \(R^2\) |
|---------------|----------|---------|
| in 0.5 H₂SO₄  | Langmuir | 0.9706  |
|               | Freundlich | 0.5882  |
|               | Temkin   | 0.7285  |
|               | Frumkin  | 0.9979  |
| in 1.0 M H₂SO₄| Langmuir | 0.9515  |
|               | Freundlich | 0.4410  |
|               | Temkin   | 0.6193  |
|               | Frumkin  | 0.9884  |
| in 1.5 M H₂SO₄| Langmuir | 0.9443  |
|               | Freundlich | 0.5890  |
|               | Temkin   | 0.7574  |
|               | Frumkin  | 0.9922  |
| in 2.0 M H₂SO₄| Langmuir | 0.9186  |
|               | Freundlich | 0.6936  |
|               | Temkin   | 0.8691  |
|               | Frumkin  | 0.9973  |

Figure 9. Langmuir (a–d), Freundlich (e–h), Temkin (i–l) and Frumkin isotherm (m–p) for the adsorption of the inhibitor on 304 SS surface in 0.5 M, 1.0 M, 1.5 M and 2.0 M H₂SO₄, respectively.
Table 6. The thermodynamic parameters for inhibitor adsorption on the 304 SS surface at ambient temperature (25 °C).

| Systems       | \( a \) | \( \log K_{ads} \) | \( \Delta G^\circ_{ads}(kJ/mol) \) | \( \Delta H^\circ_{ads}(kJ/mol) \) | \( \Delta S^\circ_{ads}(J/mol K) \) |
|---------------|--------|-----------------|--------------------------------|--------------------------------|--------------------------------|
| in 0.5 H\(_2\)SO\(_4\) | 4.586 | 3.191           | −35.301                          | −18.195                        | 57.40                          |
| in 1 M H\(_2\)SO\(_4\) | 3.976 | 2.650           | −32.216                          | −15.110                        | 57.40                          |
| in 1.5 M H\(_2\)SO\(_4\) | 3.613 | 2.383           | −30.694                          | −13.588                        | 57.40                          |
| in 2 M H\(_2\)SO\(_4\) | 3.086 | 1.932           | −28.123                          | −11.016                        | 57.41                          |

\( K_{ads} \) is related to the Gibbs free energy of adsorption (\( \Delta G^\circ_{ads} \)) by the Equation (6) [14].

\[ \Delta G^\circ_{ads} = -RT \ln(K_{ads} \times A) \]  

(6)

where \( A \) is the concentration of water (55.5 in M or 1000 in g/L), \( T \) is the absolute temperature and \( R \) is the universal gas constant.

The thermodynamic parameters are summarized in Table 6. The negative and lower values of \( \Delta G^\circ_{ads} \) indicate the inhibition process of the inhibitor on the 304 SS surface, which is spontaneous, and physisorption [13,31]. The more negative value follows the order 0.5 M H\(_2\)SO\(_4\) > 1.0 M H\(_2\)SO\(_4\) > 1.5 M H\(_2\)SO\(_4\) > 2.0 M H\(_2\)SO\(_4\).

The heat of adsorption (\( \Delta H^\circ_{ads} \)) is calculated using the Van’t Hoff equation:

\[ \ln K_{ads} = -\frac{\Delta H^\circ_{ads}}{RT} \]  

(7)

The entropy of adsorption (\( \Delta S^\circ_{ads} \)) can be obtained using Equation (8).

\[ \Delta G_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \]  

(8)

The negative value of \( \Delta H^\circ_{ads} \) confirms the exothermic nature of the metal dissolution process with the inhibitor [31]. The positive value of \( \Delta S^\circ_{ads} \) means the adsorption process is accompanied by an increase in entropy [18].

3.6. Surface Analysis

In order to provide physical evidence, SEM analysis was conducted. The impact of the inhibitor on the microstructure of the top surface of 304 SS is depicted in Figure 10. The surface of 304 SS is relatively smooth before the corrosion process (Figure 10a). After being corroded in acid solutions in the absence of the inhibitor, some cracks and pits appear on the 304 SS surface (Figure 10b); meanwhile, in the presence of the inhibitor, there is less damage (Figure 10c–f). It shows that the inhibitor works well at protecting against corrosion.
4. Conclusions

The honeycomb waste extracts can be used as an effective inhibitor for 304 SS corrosion in H2SO4 solutions. The FTIR spectrum indicates that the extract has several functional groups which are typical for a flavonoid compound. Furthermore, LC–MS analysis shows that the main compound of the extract was quercetin. The IEP% maximum in this study was obtained by adding 2000 mg/L inhibitors in 0.5 M H2SO4, that is, 97.29% using potentiodynamic polarization. The extracts adsorption behavior of the extracts follow the Frumkin isotherm model. The corrosion inhibition performance of the extracts on the surface of 304 SS decreases with acid concentration.

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