Original Article

Inhibition effect of bamboo leaves extract on cold rolled steel in Cl₃CCOOH solution

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ARTICLE INFO

Article history:
Received 30 January 2016
Accepted 14 September 2016
Available online 9 November 2016

Keywords:
Corrosion inhibitor
Trichloroacetic acid
Steel
Bamboo leaves extract
Flavonoids adsorption

ABSTRACT

The corrosion inhibition by Dendrocalamus brandisii leaves extract (DBLE)/major flavonoid of cold rolled steel (CRS) in trichloroacetic acid (Cl₃CCOOH) solution was investigated by weight loss, electrochemical techniques and atomic force microscope (AFM). The adsorption mode of four major compounds (rutin, vinent, isoviventin and orientin) on Fe (001) surface was theoretically investigated by molecular dynamics (MD). The results show that DBLE is a good inhibitor, and the maximum inhibition efficiency is higher than 95%. The adsorption of DBLE on CRS surface obeys Langmuir isotherm with exothermic process. DBLE behaves as a mixed inhibitor. AFM results confirm that DBLE could retard the corrosion of CRS in Cl₃CCOOH. The inhibitive action of each flavonoid is lower than DBLE, and follows the order:rutin > vinent > isovinentin > orientin. The major flavonoids in DBLE are adsorbed onto Fe (001) surface through FBS (flavones backbone structure) with a nearby flat orientation.

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1. Introduction

Using inhibitors is one of the most practical methods for metals protection against corrosion, especially in acid media [1]. With more and more restrictive environmental regulations, the research in the field of corrosion inhibitors has been addressed toward the goal of using cheap and effective compounds at low or “zero” environmental impact. Biodegradable plant extract could be obtained by simple extraction process from rich natural resources. Thus, the main advantage of using plant extracts as corrosion inhibitors are both economic and environmental.

Up to now, many plant extracts have been reported as effective corrosion inhibitors of steel in inorganic acids (HCl, H₂SO₄, H₃PO₄), such as henna [2,3], Nypa fruticans Wurmb [4], Zanthoxylum alatum [5], Mentha pulegium [6], olive [7], Phyllanthus amarus [8], Danssissa [9], Occimum viridis [10,11], Murraya koenigii [12], lupine [13], Ananas comosus [14], Lasiandra africana [15], Strynchos nux-vomica [16], Justicia gendarussa [17], Oxandra asbeckii [18], Ferula assa-foetida [19], coffee [20], fruit peel [21], Halfabar [22], Kopsia Singapurensis [23], Jasminum nudiflorum [24], ginkgo [25], Artemisia pallens [26], Salvia officinalis [27], Osmanthus fragrans [28], Uncaria gambir [29], garlic peel [30], Neolamarckia cadamba [31], Z. alatum [32], Acylpyra indica L. [33], Acer truncatum [34], Acer buergerianum [35], Tagetes erecta
It is found that the inhibition performance of plant extract is normally ascribed to the presence in their composition of complex organic species like tannins, alkaloids and nitrogen bases, carbohydrates, amino acids, proteins and hydrolysis products. These organic compounds always contain the adsorption centers of polar functional groups with N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures.

However, there have been lower attentions for plant extracts as corrosion inhibitors in organic acid medium. In 2012, *Piper nigrum* L. leaves extract [39] was reported as an effective corrosion inhibitor for steel in citric acid (H$_3$C$_6$H$_5$O$_7$). As another frequently used organic acid, trichloroacetic acid (Cl$_3$CCOOH) is widely used in cellulose industry [40], and in the production of TCA Na-salt used as an herbicide. Cl$_3$CCOOH shows strong corrosiveness on metal, so there is a great need to add inhibitor to protect metals in Cl$_3$CCOOH solution [40]. In 1974, Sampat and Vora [41] investigated the corrosion inhibition of aluminum in Cl$_3$CCOOH by some methyl pyridine derivatives. Since the 21st Century, xylene orange [40], amino acetonilides [42], sulphathiazole [43] and 2-acetylphenothiazine [44] have been reported as effective inhibitors for aluminum in Cl$_3$CCOOH solution. However, after carefully checking out the published references, there is almost no report about the corrosion inhibition of steel in Cl$_3$CCOOH solution, specially for plant extract inhibitors.

In our laboratory, much work has been conducted to study the inhibition by bamboo leaves extract on the corrosion of metals in various media. The main reason is that bamboo leaves are abundant resources (about 1200 species and 70 genera of bamboo in the world) with fast and continuous renewal. Most important of all, bamboo leaves extract is virtually nonpoisonous [45,46]. Recently, the bamboo leaves extracts have been reported as good inhibitors for steel in HCl [47,48] and in H$_3$C$_6$H$_5$O$_7$ [49] media. In continuation of our previous study, the present work firstly reports the inhibition effect of *Dendrocalamus brandisii* leaves extract (DBLE) on the corrosion of cold rolled steel (CRS) in Cl$_3$CCOOH solution by weight loss, polarization curves and electrochemical impedance spectroscopy (EIS) methods. The steel surface was characterized by AFM technique. Meanwhile, molecular dynamics (MD) was applied to theoretically elucidate the adsorption mode of major flavonoid molecule (rutin, vintin, isoventin, orientin) on Fe (001) surface. The electrochemical corrosion mechanism of steel in Cl$_3$CCOOH solution is proposed. Lastly, the inhibitive mechanism of DBLE is presented according to the difference in inhibition performance between DBLE and major flavonoid.

### 2. Experimental

#### 2.1. Materials

Tests were conducted on CRS having composition (wt.%): 0.07% C, 0.3% Mn, 0.022% P, 0.010% S, 0.011% Si, 0.030% Al and the remainder Fe. Trichloroacetic acid (Cl$_3$CCOOH) is of analytical reagent (AR) grade, and four major compounds (rutin, vintin, isoventin and orientin) are of pure standards. All of these chemical reagents are obtained from Shanghai Chemical Reagent Company of China. The aggressive solutions of 0.05–0.5 M Cl$_3$CCOOH were prepared by dilution of AR grade Cl$_3$CCOOH with distilled water. The ionization equilibrium constant (K$_a$) of Cl$_3$CCOOH is $2.2 \times 10^{-1}$ ($pK_a = 0.66$, 20 °C). The experimentally measured and calculated pH values are listed in Table 1; clearly in good agreement with the theoretically calculated pH values.

<table>
<thead>
<tr>
<th>pH (Cl$_3$CCOOH)</th>
<th>Measured pH</th>
<th>Calculated pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 M</td>
<td>1.34</td>
<td>1.38</td>
</tr>
<tr>
<td>0.1 M</td>
<td>1.10</td>
<td>1.13</td>
</tr>
<tr>
<td>0.2 M</td>
<td>0.85</td>
<td>0.95</td>
</tr>
<tr>
<td>0.3 M</td>
<td>0.74</td>
<td>0.77</td>
</tr>
<tr>
<td>0.4 M</td>
<td>0.66</td>
<td>0.69</td>
</tr>
<tr>
<td>0.5 M</td>
<td>0.57</td>
<td>0.62</td>
</tr>
</tbody>
</table>

DBLE was extracted from *D. brandisii* leaves using 80% (percent by volume) C$_2$H$_5$OH water solution at 75 °C for 2 h in our laboratory, as described in our earlier work [48,50]. The production rate is about 9.7%. Fourier transform infrared spectroscopy (FTIR) of DBLE and the average content of total flavonoids in DBLE (about 28%) were fully studied in our recent paper [48]. The concentration range of DBLE was 10–200 mg l$^{-1}$.

#### 2.2. Weight loss and electrochemical measurements

CRS sheets of 2.5 cm $\times$ 2.0 cm $\times$ 0.06 cm were abraded by a series of emery paper (grade 320–500–800) and then washed with distilled water and degreased with acetone. The weight loss and electrochemical measurements have been described in detail in our earlier reports [47–50]. The immersion time of weight loss is 3–34 h, and the experimental temperature is 20–50 °C. Electrochemical experiments were carried out using a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research) with a conventional three-electrode system: counter electrode (platinum), reference electrode (saturated calomel electrode (SCE)) coupled to a fine Luggin capillary and working electrode (surface area is 1.0 cm $\times$ 1.0 cm).

For the weight loss method, the corrosion rate ($v$) was calculated from the following equation:

$$ v = \frac{W}{St} \quad (1) $$

where $W$ is the average weight loss of two parallel CRS sheets (g), $S$ the total area of one CRS specimen (m$^2$), and $t$ is the immersion time (h). With the calculated corrosion rate, the inhibition efficiency ($\eta_w$) was calculated as follows:

$$ \eta_w = \frac{v_0 - v}{v_0} \times 100 \quad (2) $$

where, $v_0$ and $v$ are the values of corrosion rate without and with inhibitor, respectively.

Before electrochemical measurements, the electrode was immersed in test solution at open circuit potential (OCP) for 2 h at 20 °C to reach a stable state. The potentiodynamic polarization curves were carried out by polarizing to $\pm 250$ mV vs.
OCP at a sweep rate of 0.5 mV s\(^{-1}\). Inhibition efficiency \(\eta_p\) is calculated through the corrosion current density \(i_{corr}\) values [47]:

\[
\eta_p = \frac{i_{corr} - i_{corr(\text{inh})}}{i_{corr}} \times 100\%
\]  

(3)

where \(i_{corr}\) and \(i_{corr(\text{inh})}\) represent corrosion current density values without and with inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) was carried out at stable OCP (no extra bias voltage, 2 h of immersion) over a frequency range from 100 kHz to 10 mHz using a 10 mV root mean square (r.m.s) voltage excitation. The total number of points is 30. Inhibition efficiency \(\eta_p\) is estimated by the relation below [47]:

\[
\eta_R = \frac{R_{(\text{inh})} - R_{(\text{no})}}{R_{(\text{no})}} \times 100\%
\]  

(4)

where \(R_{(\text{no})}\) and \(R_{(\text{inh})}\) are charge transfer resistance values in the absence and presence of the inhibitor, respectively.

2.3. Atomic force microscope (AFM)

The CRS specimens of 1.5 cm \(\times\) 1.0 cm \(\times\) 0.06 cm were prepared as described above (Section 2.2). After immersion in 0.1 M \(\text{Cl}_2\text{CCOOH}\) solutions without and with 200 mg l\(^{-1}\) DBLE at 20 °C for 6 h, the specimens were cleaned with distilled water, dried with a cold air blaster, and then used for a Japan instrument model SPA-400 SPM Unit atomic force microscope (AFM) examinations. The AFM images were measured in tapping mode using Si\(_3\)N\(_4\) tips.

2.4. MD simulations

MD simulations were performed with Discover program in Materials Studio 4.1 software from Accelrys Inc. [51]. According to many MD studies about the adsorption of inhibitor on steel surface [52, 53], there could be strong interaction between organic inhibitor and Fe (001) surface, so Fe (001) surface is chosen to study. Fe (001) plane was firstly cleaved from pure Fe crystal, the surface was then optimized to the energy minimum, and then was enlarged to fabricate an appropriate supercell. After that, a vacuum slab with 1 Å thickness was built above the Fe (001) supercell with 31.53 Å \(\times\) 31.53 Å \(\times\) 15.30 Å of total 1331 Fe atoms. Meanwhile, the optimized inhibitor molecules of rutin, vinitin, isovin-entin and orientin were done with DMol\(^3\) numerical based density function theory (DFT) in Materials Studio 4.1 at PW91/DNP/COSMO level [54, 55], and then the inhibitor layers were built using the Amorphous cell program. Finally, the adsorption system was built by layer builder to place the inhibitor layer to Fe (001) supercell. All these slabs are separated by a 10 Å vacuum thickness to ensure that the interaction between the periodically repeated slabs along the normal of the surface is small enough. The adsorption system was optimized using COMPASS force field. The MD simulation was performed under 298 K, NVT ensemble, with a time step of 1.0 fs and simulation time of 1000 ps.

Both adsorption energy \(E_{\text{ads}}\) and binding energy \(E_{\text{bin}}\) could determine the stability of inhibitor on metal surface. They have different view angles. \(E_{\text{ads}}\) is mainly used to study the adsorption of inhibitor on the metal surface, and it is calculated as follows [56]:

\[
E_{\text{ads}} = (E_{\text{inh}} + E_{\text{surf}}) - E_{\text{total}}
\]  

(5)

where \(E_{\text{inh}}\) and \(E_{\text{surf}}\) are the energies of the free inhibitor molecule and Fe (001) plane, respectively. \(E_{\text{total}}\) is the total energy of Fe (001) plane together with inhibitor molecule adsorbed on the iron surface.

On the other hand, \(E_{\text{bin}}\) is mainly focused on the interaction between inhibitor and metal surface, and it could be calculated by means of the following relationship:

\[
E_{\text{bin}} = E_{\text{total}} - (E_{\text{inh}} + E_{\text{surf}})
\]  

(6)

Comparing Eq. (5) with (6), it is evident that \(E_{\text{bin}}\) is the negative value of the \(E_{\text{ads}}\) [57]:

\[
E_{\text{bin}} = -E_{\text{ads}}
\]  

(7)

3. Results and discussion

3.1. Weight loss measurements

The weight loss method is widely used to quantitatively determine corrosion rate \(\nu\) and inhibition efficiency \(\eta_w\) owing to its good reliability. For the present study, the relative phase difference (RPD) \(\nu\) and \(\eta_w\) for two parallel specimens are less than 5%, which confirms that the reproducibility for the present system is very precise.

3.1.1. Effect of DBLE concentration on inhibition efficiency

The corrosion rates in 0.1M \(\text{Cl}_2\text{CCOOH}\) solution without inhibitor are 20.37 (RPD = 1.6%) g m\(^{-2}\) h\(^{-1}\) at 20 °C, 40.90 (RPD = 1.9%) g m\(^{-2}\) h\(^{-1}\) at 30 °C, 58.48 (RPD = 2.0%) g m\(^{-2}\) h\(^{-1}\) at 40 °C, and 72.60 (RPD = 2.2%) g m\(^{-2}\) h\(^{-1}\) at 50 °C, which indicates that CRS is severely corroded by \(\text{Cl}_2\text{CCOOH}\) acid. When DBLE is added to the \(\text{Cl}_2\text{CCOOH}\) media, the corrosion of CRS is retarded prominently. Fig. 1 presents \(\eta_w\) for different DBLE concentrations (10–200 mg l\(^{-1}\)) in 0.1M \(\text{Cl}_2\text{CCOOH}\) solutions at 20–50 °C. Clearly, \(\eta_w\) increases with the inhibitor concentration at all temperatures studied. \(\eta_w\) increases remarkably with DBLE concentration from 10 to 100 mg l\(^{-1}\), but a further raise in inhibitor concentration causes no appreciable change in inhibitive performance. The maximum \(\eta_w\) at 200 mg l\(^{-1}\) is 96.1% (RPD = 2.3%) at 20 °C; 94.2% (RPD = 2.3%) at 30 °C; 90.4% (RPD = 2.4%) at 40 °C; and 85.8% (RPD = 2.5%) at 50 °C. Thus, DBLE acts as a good inhibitor for CRS in \(\text{Cl}_2\text{CCOOH}\) media. According to our recent work, bamboo leaves extract acts as the good corrosion inhibitor for CRS in \(\text{HCl}\) [47, 48], \(\text{H}_2\text{SO}_4\) [47] and \(\text{H}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}\) [49], which implies that the bamboo leaves extract could be seemed as the good potential corrosion inhibitor for steel in either inorganic acid or organic acid solution.

Also, Fig. 1 illustrates that \(\eta_w\) decreases to some extent with the elevated temperature within whole inhibitor
concentrations from 10 to 200 mg l\(^{-1}\), which would be attributed to the DBLE desorption from the CRS surface due to the higher temperatures.

3.1.2. Adsorption isotherm

Acid inhibitor generally exhibits inhibitive performance through adsorption on metal surface, and some adsorption isotherms have been widely used to study the adsorption behavior. In previous studies of bamboo leaves extract as corrosion inhibitors for steel in acids [47-49], the adsorption of bamboo leaves extract on steel surface follows Langmuir adsorption isotherm. For the present study, Langmuir adsorption isotherm is also applied to study the adsorption of DBLE on steel surface in CCl\(_3\)COOH solution [58]:

\[
\frac{c}{\theta} = \frac{1}{K} + c
\]

(8)

where \(c\) is the concentration of inhibitor (mg l\(^{-1}\)), \(K\) the adsorptive equilibrium constant (l mg\(^{-1}\)), and \(\theta\) is the surface coverage with the value of inhibition efficiency (\(\eta_{\theta}\)) [58].

The straight lines of \(c/\theta\) vs. \(c\) at four temperatures are shown in Fig. 2, and the corresponding linear regression parameters are given in Table 2. All linear correlation coefficients \(r\) are almost equal to 1, and the slope values are also close to 1,

so the adsorption of DBLE on CRS surface obeys the Langmuir adsorption isotherm. Larger value of \(K\) generally means stronger adsorptive ability and hence better inhibitive ability of a given inhibitor. As shown in Table 2, \(K\) decreases with an increase of the temperature, which implies that it is easy for DBLE to be adsorbed onto the steel surface in CCl\(_3\)COOH solution at relatively low temperature. On the other hand, the adsorbed inhibitor molecules tend to desorb from the metal surface, giving rise to severe corrosive attack at high temperature.

### Table 2 – Parameters of the linear regression between \(c/\theta\) and \(c\) in 0.1 M CCl\(_3\)COOH solution.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(r)</th>
<th>Slope</th>
<th>(K) (l mg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.9999</td>
<td>1.01</td>
<td>0.15643</td>
</tr>
<tr>
<td>30</td>
<td>0.9994</td>
<td>0.98</td>
<td>0.06886</td>
</tr>
<tr>
<td>40</td>
<td>0.9948</td>
<td>0.91</td>
<td>0.02936</td>
</tr>
<tr>
<td>50</td>
<td>0.9902</td>
<td>0.87</td>
<td>0.01883</td>
</tr>
</tbody>
</table>

3.1.3. Effect of immersion time on corrosion inhibition

Fig. 3 shows the inhibition efficiency (\(\eta_{\theta}\)) values of 200 mg l\(^{-1}\) DBLE for different immersion time (\(t\)) at 20 °C in 0.1 M CCl\(_3\)COOH using weight loss method. \(\eta_{\theta}\) increases with immersion time from 3 to 6 h, thereafter remains almost stable from 6 to 24 h, and \(\eta_{\theta}\) is as high as 97.3% even when the immersion is as long as 24 h. Similar results were also previously reported for bamboo leaves extract as the corrosion inhibitor for HCl and H\(_2\)SO\(_4\) solutions [47]. This behavior could be attributed to the adsorptive film of inhibitor that rests upon the immersion time [47]. The inhibitive film on steel surface firstly reaches a more compact and uniform condition during prolonging immersion time (3-6 h), while the adsorptive film is in a saturated state within 6-24 h.

3.1.4. Effect of acid concentration on corrosion inhibition

Fig. 4 shows the relationship between corrosion rate (\(v\)) and CCl\(_3\)COOH concentration (\(C\)) at 20 °C (immersion time is 6 h). It is of interest to note that the corrosion rate increases linearly with the increase of CCl\(_3\)COOH concentration from 0.05 to 0.5 M either in the absence or presence of 200 mg l\(^{-1}\) DBLE. This unique result of steel in CCl\(_3\)COOH is quite different from that of steel in inorganic acids (HCl, H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\)) [59].
When 200 mg l\(^{-1}\) DBLE is added to Cl\(_3\)COOH solution, the corrosion rate decreases sharply. This confirms that DBLE exhibits good inhibitive performance in the whole acid concentration studied. In 0.5 M Cl\(_3\)COOH solution without inhibitor, the corrosion rate reaches as high as 118.56 g m\(^{-2}\) h\(^{-1}\), while it is decreased to 1.68 g m\(^{-2}\) h\(^{-1}\) in the presence of 200 mg l\(^{-1}\) DBLE.

Fig. 5 illustrates the dependence of inhibition efficiency (\(\eta_i\)) on the concentration of Cl\(_3\)COOH (0.05–0.5 M) at 20 °C. Clearly, \(\eta_i\) increases slightly with the concentration of Cl\(_3\)COOH from 91.3% to 98.6% with respect to 0.05 M and 0.5 M. The reason might be due to the more protective film by the interaction of the inhibitor molecules with Fe\(^{2+}\) [60] or protonated inhibitor molecules with acid anion (Cl\(_3\)COO\(^-\)) at higher acid concentration.

### 3.2. Open circuit potential (OCP) – time curves

Fig. 6 shows OCP as a function of time (0–180 min) in 0.1 M Cl\(_3\)COOH solution without and with 200 mg l\(^{-1}\) DBLE at 20 °C. For both cases, OCP initially moves positive value along with time and reaches the peak at about 20 min, and then shifts to negative and gradually reaches steady state from 60 to 180 min. The potentiodynamic polarization curves and electrochemical impedance spectroscopy (see later) were carried out with OCP in a steady state with immersion time of 2 h, and OCP values are −409 mV and −398 mV vs. SCE in the absence and presence of 200 mg l\(^{-1}\) DBLE, respectively.

### 3.3. Potentiodynamic polarization curves of DBLE

Potentiodynamic polarization curves of CRS in 0.1 M Cl\(_3\)COOH containing 0, 10, 50, 100 and 200 mg l\(^{-1}\) DBLE at 20 °C (immersion time is 2 h) are shown in Fig. 7. As compared to that of the blank solution, the presence of DBLE causes the decrease in the corrosion rate of CRS in 0.1 M Cl\(_3\)COOH, i.e., shifts both cathodic curves and the anodic curves toward lower current densities. The shift of polarization curves toward the lower current density region is much more pronounced when the concentration of DBLE is increased. The results indicate that both cathodic and anodic reactions of CRS electrode corrosion in Cl\(_3\)COOH solution are retarded by DBLE. Namely, DBLE could be arranged as a mixed-type inhibitor. The nature of polarization curves remains the same irrespective of different concentration of DBLE addition to acid solution, which suggests that the mechanism for the corrosion of steel in Cl\(_3\)COOH solution does not change by adding DBLE to the acid solution.

Inspection of Fig. 7 reveals that the cathodic polarization curves display three portions (I, II, and III), which indicates that there are both activation controlled and diffusion
controlled regions for the cathodic polarization curves. Portion I might be related to the reduction of trichloroacetic acid in strong cathodic polarization region (about −0.70 to −0.65 V vs. SCE). Portion II would be related to the reduction of O₂ in diffusion region (about −0.65 to −0.55 V vs. SCE). Portion III represents the evolution of hydrogen in activation controlled region (about −0.55 V vs. SCE to OCP). In a word, there are a series of complex cathodic reduction reactions in Cl₃CCOOH solution. Cl₃CCOOH would be dissociated to H⁺ and Cl₃CCOO⁻ in water solution. According to the proposed mechanism of steel in acid solution [61], the cathodic hydrogen evolution reaction follows the steps (9)–(12):

Fe + H⁺ ↔ (FeH⁺)ads  
(9)

(FeH⁺)ads + e⁻ ↔ (FeH)ads  
(10)

(FeH)ads + H⁺ + e⁻ ↔ Fe + H₂  
(11)

Two (FeH)ads may combine together to liberate hydrogen as following [62]:

(FeH)ads + (FeH)ads ↔ 2Fe + H₂  
(12)

The anion of Cl₃CCOOH (Cl₃CCOO⁻) might also react with H⁺ to produce HCl₃CCOO⁻ and H₂Cl₃CCOO⁻ [63]:

Cl₃CCOO⁻ + H⁺ + 2e⁻ → HCl₃CCOO⁻ + Cl⁻  
(13)

HCl₃CCOO⁻ + H⁺ + 2e⁻ → H₂Cl₃CCOO⁻ + Cl⁻  
(14)

For anodic polarization curves as shown in Fig. 7, it is worth noting that two portions (IV and V) are observed, which represent the weak polarization region (OCP to −0.35 V vs. SCE) and strong polarization region (−0.35 to −0.15 V vs. SCE), respectively. According to the mechanism for the corrosion of mild steel in aqueous solutions of formic acid (HCOOH) [62], acetic acid (CH₃COOH) [64] and peracetic acid (CH₃OOH) [65], the anodic dissolution of CRS in Cl₃CCOOH solutions may be assumed as follows:

Fe + Cl₃CCOO⁻ → (FeCl₃CCOO⁻)ads  
(15)

(FeCl₃CCOO⁻)ads → (FeCl₃CCOO)ads + e⁻  
(16)

(FeCl₃CCOO)ads → (FeCl₃CCOO⁺) + e⁻  
(17)

FeCl₃CCOO⁺ → Fe²⁺ + Cl₃CCOO⁻  
(18)

Thus, the adsorption of Cl₃CCOO⁻ ions on the CRS surface would be the prerequisite for the anodic dissolution to occur.

The electrochemical parameters of corrosion current densities (icorr), corrosion potential (Ecorr), cathodic Tafel slope (bₐ) and anodic Tafel slope (bₐ) are obtained by using electrochemistry powersuite software to fit weak polarization curves of Tafel polarization in the optimum linear regions of III and IV. Inhibition efficiency (ηp) values are calculated through icorr and summarized in Table 3. The presence of DBLE shifts Ecorr to positive to some extent, but the maximum change of Ecorr is lower than 85 mV. Therefore, DBLE could be classified as a mixed-type inhibitor [66,67]. Clearly, icorr decreases prominently in the presence of DBLE, while ηp increases with the inhibitor concentration, and the maximum ηp reaches as high as 97.2%, which indicates that DBLE acts as a good inhibitor in Cl₃CCOOH. Tafel slopes of bₐ and bₐ change upon addition of DBLE, which means that the inhibitor molecules are adsorbed on both the anodic and cathodic sites resulting in the changing rules of the potential with current densities.

3.4. Electrochemical impedance spectroscopy (EIS)

Fig. 8 shows the Nyquist diagrams of CRS obtained at OCP (immersion time: 2 h) in 0.1 M Cl₃CCOOH without and with different concentrations of DBLE at 20 °C. It appears as a large capacitive loop at high frequency (HF) followed also by an inductive one at low frequency (LF) values. Comparing with 0.1 M Cl₃CCOOH solution in the absence of inhibitor, the general shape is maintained for all tested concentrations, indicating that almost no change in the corrosion mechanism occurs as a result of the inhibitor addition [68]. In addition, the diameter of the capacitive loop in the presence of DBLE is bigger than that in blank solution and increases with the inhibitor concentration. This indicates that the impedance of inhibited substrate increases with the concentration of inhibitor.

The Bode modulus and phase angle plots for CRS in 0.1 M Cl₃CCOOH containing different concentrations of DBLE are given in Fig. 9. As can be seen from Fig. 9(a), the increase of absolute impedance at low frequencies in Bode modulus confirms the higher protection with increasing the concentration of DBLE, which is related to the adsorption of the inhibitor molecules on the CRS surface. Also from Fig. 9(b), there are one phase peak at high frequency and one valley at low frequency, which again confirms that there are two time constants related to respective capacitive loop and inductive loop.

The capacitive loop at HF is usually related to the charge transfer of the corrosion process and double layer behavior. These capacitive loops at HF are depressed semicircles shown in Nyquist plots and the phase angle is lower than 90° in Bode phase plots, which could be attributed to the frequency dispersion as a result of the roughness and inhomogeneous of
electrode surface [68]. On the other hand, the cause of the inductive loop is still uncertain. The relaxation of adsorbed charged intermediates may result in the inductive loop [69]. This is more pronounced when the intermediates are strongly adsorbed. The relaxations of adsorbed species include H$_{ads}^+$ [70], acid anions [71] or inhibitor species [30] on the electrode surface.

The EIS results in Cl$_3$CCOOH solutions are simulated by the equivalent circuits shown in Fig. 10. $R_s$, $R_i$ and $R_L$ are the solution resistance, charge transfer resistance and inductive resistance, respectively. CPE is a constant phase element. $L$ is the inductance, which is intimately associated with the inductive loop. The solid lines in Figs. 8 and 9 correspond to the fitted plots for EIS experiment data using the electric circuit of Fig. 10, which indicates that the experimental data could be simulated using this equivalent circuit. The impedance parameters of CRS in Cl$_3$CCOOH solution are listed in Table 4. The chi-squared ($\chi^2$) is used to evaluate the precision of the fitted data [72,73]. Table 4 reveals that $\chi^2$ values are low, which indicates that the fitted data have good agreement with the experimental data. It is observed that $R_s$ is about 6–10 $\Omega$ cm$^2$ in 0.1 M Cl$_3$CCOOH, while the $R_i$ is less than 0.5 $\Omega$ cm$^2$ for steel in 1.0 M HCl and 0.5 M H$_2$SO$_4$ solutions [47,48]. This implies that 0.1 M Cl$_3$CCOOH water solution is not very conductive. $R_i$ is increased to more extent when DBLE is added to the 0.1 M Cl$_3$CCOOH solution, which indicates the electrode exhibits slower corrosion in the presence of the plant inhibitor of DBLE. In contrast, the decrease of CPE in the presence of DBLE comparing with that in blank Cl$_3$CCOOH solution (without inhibitor) results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. In other words, the inhibitor molecules function by adsorption at the metal/solution interface [67]. The exponent $n$ of CPE is usually used to study the change in interfacial surface condition of steel/solution. Inspection of Table 4 reveals that $n$ is around 0.8, which might be resulted from irregular surface of electrode or arbitrary distribution of current on electrode surface causing frequency dispersion.

Table 3 – Potentiodynamic polarization parameters for the corrosion of CRS in 0.1 M Cl$_3$CCOOH solution containing different concentrations of DBLE at 20°C (immersion time is 6 h).

<table>
<thead>
<tr>
<th>$c$ (mg l$^{-1}$)</th>
<th>$E_{corr}$ (mV vs. SCE)</th>
<th>$i_{corr}$ (µA cm$^{-2}$)</th>
<th>$-b_C$ (mV dec$^{-1}$)</th>
<th>$b_s$ (mV dec$^{-1}$)</th>
<th>$n_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−418.1 ± 2.9</td>
<td>1386.8 ± 19</td>
<td>181 ± 4</td>
<td>51 ± 6</td>
<td>−</td>
</tr>
<tr>
<td>10</td>
<td>−385.3 ± 2.5</td>
<td>628.2 ± 12</td>
<td>178 ± 3</td>
<td>31 ± 7</td>
<td>54.7</td>
</tr>
<tr>
<td>50</td>
<td>−398.5 ± 2.1</td>
<td>222.7 ± 13</td>
<td>152 ± 4</td>
<td>30 ± 6</td>
<td>83.9</td>
</tr>
<tr>
<td>100</td>
<td>−388.7 ± 3.4</td>
<td>108.6 ± 8</td>
<td>138 ± 3</td>
<td>27 ± 4</td>
<td>92.2</td>
</tr>
<tr>
<td>200</td>
<td>−389.5 ± 2.6</td>
<td>38.3 ± 10</td>
<td>119 ± 3</td>
<td>24 ± 4</td>
<td>97.2</td>
</tr>
</tbody>
</table>

Fig. 9 – Bode plots of the corrosion of CRS in 0.1 M Cl$_3$CCOOH without and with different concentrations of DBLE at 20°C (immersion time is 2 h): (a) Bode modulus; and (b) Bode phase angle plots.

---

**Table 4**

<table>
<thead>
<tr>
<th>$c$ (mg l$^{-1}$)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_i$ (Ω cm$^2$)</th>
<th>$L$ (mH cm$^2$)</th>
<th>$CPE$</th>
<th>$\chi^2$</th>
<th>$n_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.7 ± 1.2</td>
<td>12.7 ± 1.2</td>
<td>8.9 ± 0.8</td>
<td>0.091</td>
<td>2.1</td>
<td>6.3</td>
</tr>
<tr>
<td>10</td>
<td>10.2 ± 1.6</td>
<td>10.2 ± 2.0</td>
<td>7.3 ± 1.1</td>
<td>0.089</td>
<td>1.9</td>
<td>6.8</td>
</tr>
<tr>
<td>50</td>
<td>51.7 ± 3.2</td>
<td>71.8 ± 4.3</td>
<td>34.8 ± 2.4</td>
<td>0.102</td>
<td>1.2</td>
<td>5.7</td>
</tr>
<tr>
<td>100</td>
<td>133.0 ± 5.6</td>
<td>217.4 ± 8.9</td>
<td>103.4 ± 6.3</td>
<td>0.105</td>
<td>0.9</td>
<td>5.4</td>
</tr>
<tr>
<td>200</td>
<td>256.8 ± 10.1</td>
<td>427.6 ± 15.3</td>
<td>217.4 ± 10.5</td>
<td>0.107</td>
<td>0.7</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Fig. 10 – Equivalent circuit used to fit the EIS.
Table 4 – EIS parameters for the corrosion of CRS in 0.1 M Cl$_3$CCOOH containing DBLE at 20 °C.

<table>
<thead>
<tr>
<th>c (mg l$^{-1}$)</th>
<th>$R_0$ (Ω cm$^2$)</th>
<th>$R_t$ (Ω cm$^2$)</th>
<th>$R_C$ (Ω cm$^2$)</th>
<th>CPE (μF cm$^{-2}$)</th>
<th>n</th>
<th>L (H cm$^2$)</th>
<th>$\chi^2$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.27 ± 0.06</td>
<td>1.62 ± 0.50</td>
<td>3.92 ± 0.80</td>
<td>433.2 ± 3.0</td>
<td>0.8401 ± 0.02</td>
<td>84 ± 4</td>
<td>5.09 × 10$^{-3}$</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>1.95 ± 0.10</td>
<td>2.20 ± 1.00</td>
<td>5.89 ± 2.00</td>
<td>233.3 ± 5.0</td>
<td>0.8251 ± 0.02</td>
<td>121 ± 10</td>
<td>6.41 × 10$^{-3}$</td>
<td>51.0</td>
</tr>
<tr>
<td>50</td>
<td>2.93 ± 0.15</td>
<td>3.89 ± 2.00</td>
<td>9.65 ± 3.00</td>
<td>179.5 ± 6.7</td>
<td>0.8021 ± 0.02</td>
<td>203 ± 12</td>
<td>9.32 × 10$^{-3}$</td>
<td>81.8</td>
</tr>
<tr>
<td>100</td>
<td>3.97 ± 0.20</td>
<td>5.89 ± 3.00</td>
<td>15.6 ± 5.00</td>
<td>96.6 ± 8.2</td>
<td>0.8187 ± 0.03</td>
<td>466 ± 14</td>
<td>2.25 × 10$^{-2}$</td>
<td>91.6</td>
</tr>
<tr>
<td>200</td>
<td>5.01 ± 0.25</td>
<td>7.89 ± 4.00</td>
<td>23.6 ± 9.00</td>
<td>96.9 ± 9.2</td>
<td>0.7977 ± 0.03</td>
<td>467 ± 13</td>
<td>5.79 × 10$^{-2}$</td>
<td>94.0</td>
</tr>
</tbody>
</table>

Fig. 11 – AFM three-dimensional images of CRS surface: (a) before immersion; (b) after 6 h of immersion at 20 °C in 0.1 M Cl$_3$CCOOH; and (c) after 6 h of immersion at 20 °C in 200 mg l$^{-1}$ DBLE + 0.1 M Cl$_3$CCOOH.

3.5. Atomic force microscope (AFM) surface examination

AFM provides a powerful means of characterizing the microstructure [74], and is generally used in the field of metal corrosion. The three-dimensional AFM images of CRS surface are shown Fig. 11. The CRS surface before immersion seems smooth as shown in Fig. 11(a). However, it is not absolute smooth and uniform, and small precipitates appear on the steel surface, which could be attributed to some contaminates formed on AFM tip during the examination process. As for Fig. 11(b), the CRS surface after immersion in uninhibited 0.1 M Cl$_3$CCOOH for 6 h exhibits a very rough surface owing to corrosive attack by CCl$_3$COOH acid, and covered with the uneven and potholed corrosion products layer upon layer. On contrast, in the presence of 200 mg l$^{-1}$ DBLE, Fig. 11(c) shows that the steel surface appears the more flat, homogeneous and uniform, and even some original abrating scratches are seen on the steel surface, which indicates that DBLE retards efficiently the corrosion the steel in 0.1 M Cl$_3$CCOOH solution.

3.6. Corrosion inhibition of the major flavonoids

Bamboo leaves extract is composed of numerous chemical compounds, and then the inhibitive action of bamboo leaves extract would be due to the adsorption of its components on the steel surface. However, it is rather difficult to assign the inhibitive effective to a particular constituent owing to the complex chemical composition of the bamboo leaves extract. The ethanol/water extract of bamboo leaf is mainly composed of the bamboo leaf flavonoids (BLF) [75]. According to our recent work [55], there is a relation between the content
of total flavonoids and inhibition efficiency, and it might be deduced that the flavonoids would be one of the contributors to the inhibitive activity. On the other hand, the major flavonoids in bamboo leaves extract are rutin, orientin, isovientin and vientin [76,77], and their molecular structures are shown in Fig. 12. In our recent work [49,54], rutin, orientin, vientin and isovientin are confirmed in the presence of bamboo leaves extract through analyzing high performance liquid chromatography (HPLC). According to the quantum chemical calculations of rutin, orientin, vientin and isovientin in our recent work [54,55], the adsorption of flavonoids is mainly through the flavones backbone structure (FBS) whose molecular structure is shown in Figs. 12(e) and (f). Noticeably, a number of flavonoids have similar chemical molecular skeleton structure of FBS, which implies that the series of flavonoids could be seemed as the potential contributors for the inhibition performance [49].

In the present study, the inhibition action of four major components of rutin, isovientin, vientin and orientin with 200 mg l\(^{-1}\) in 0.1 M \(\text{CCl}_3\text{COOH}\) solution at 20 °C are studied, and the results are given in Fig. 13. The inhibition efficiency of these flavonoids follows the sequence: rutin > orientin > isovientin > vientin. At all temperatures, the inhibition efficiency values range from 70% to 85%, which indicates that these flavonoids could also retard to more extent the corrosion of steel in \(\text{CCl}_3\text{COOH}\) solution. Also, the inhibition efficiency decreases with the temperature.

MD simulations have been done to further study the adsorption behavior of the four flavonoids molecules of...
rutin, orientin, isovientin and vientin on the Fe (001) surface. Through the analysis of the temperature and energy, it takes about 250 ps for the adsorption system containing both Fe (001) surface and the studied inhibitor molecule to reach equilibrium. The adsorption system is at steady state and fluctuates slightly from 500 ps to 1000 ps. Fig. 14 shows the adsorption configurations on Fe (001) surface for inhibitor molecules, and the corresponding $E_{\text{ads}}$ and $E_{\text{bin}}$ values are listed in Table 5.

As can be seen from Fig. 14, these flavonoids are adsorbed on Fe (001) surface through FBS with a nearby flat orientation. In other words, the adsorption center is FBS, which is in accordance with the previous result of quantum chemical calculations [54,55]. Moreover, the values of $E_{\text{ads}}$ in Table 5 reveal the sequence of rutin > orientin > isovientin > vientin, meaning that the adsorptive ability on steel surface follows the expected trend: rutin > orientin > isovientin > vientin.

On the other hand, magnitude of $E_{\text{bin}}$ is indicative of stability of adsorptive system, and $E_{\text{bin}}$ follows the order: rutin < vientin < isovientin < orientin. More negative value of $E_{\text{bin}}$ suggests a more stable adsorption system and leads to the higher inhibitive action. Accordingly, inhibition efficiency for four studied inhibitors is ranked as rutin > orientin > isovientin > vientin based on the parameters of $E_{\text{ads}}$ and $E_{\text{bin}}$. Thus, the theoretical inference is in good agreement with experimental data.

The difference in their inhibitive action can be explained on the basis of their molecular structure. The FBS of rutin and orientin as shown in Fig. 12(e) has one additional hydroxyl group (–OH) than the FBS of isovientin and vientin as shown in Fig. 12(f). The substitution –OH is the additional center of adsorption, which causes more adsorption centers and corresponding better inhibition performance. Consequently, rutin and orientin give better inhibitive performance than isovientin and vientin. Besides the FBS, this classification of inhibition efficiency could be attributed to the difference in sugar substitute to the FBS. Rutin has the disaccharide substituents to FBS, while orientin has the monosaccharide substituent. The disaccharide substituents have more oxygen atoms, thus rutin has higher inhibitive performance than orientin. It should be noted that the substitutional group of both isovientin and vientin are the same. However, Fig. 13 shows that isovientin gives slightly better inhibitive performance than vientin. This difference in inhibition efficiency could be explained on the basis of substitution group position.

Noticeably, the inhibitory value of each flavonoid is lower than the crude extract of DBLE, which may suggest that other composition compounds have additional contribution to the inhibitive performance. The same conclusion was also reported for bamboo leaves extract as the corrosion inhibitor for steel in H$_3$PO$_4$ solution [54]. Similar comparative results between plant extract and its major component have also been reported for the coffee extract [20] and A. pallens [26]. Besides the flavonoids, the ethanol/water extract of bamboo leaf contains amino acid, chlorophyll and amylose [78], and these compounds contain many O, N atoms in functional groups (O–H, C=O, C–O, N–H) and O-heterocyclic rings. Thus, it is reasonable to deduce that these compounds get to be protonated in the acid solution. In Cl$_2$COCOOH solution, Cl$_2$COCOO$^-$ could be adsorbed onto the steel surface, then the protonated compounds approach the steel surface due to the electrostatic attraction. In addition, O, N atoms with plentiful lone electrons could be considered responsible for the adsorption centers on steel surface. Coordinate bond could be formed by partial transference of electrons from the N atoms to the metal surface.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Values of adsorption energy ($E_{\text{ads}}$) and binding energy ($E_{\text{bin}}$) between the molecules and Fe (001) planes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>$E_{\text{ads}}$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>Rutin</td>
<td>1104.35</td>
</tr>
<tr>
<td>Orientin</td>
<td>890.01</td>
</tr>
<tr>
<td>Isovientin</td>
<td>831.83</td>
</tr>
<tr>
<td>Vientin</td>
<td>830.95</td>
</tr>
</tbody>
</table>

Fig. 14 – Equilibrium adsorption configuration of inhibitors on Fe (001) planes obtained by MD simulations: (a) rutin; (b) orientin; (c) isovientin; and (d) vientin.
4. Conclusions

(1) DBLE acts as a good inhibitor for the corrosion of CRS in 0.1 M Cl₂COO⁻ solution, and $i_{hr}$ value of 120 mg l⁻¹ DBLE is higher than 94% at 20°C. Inhibition efficiency ($i_{hr}$) increases with the inhibitor concentration, immersion time and acid concentration, but decreases with the temperature. The adsorption of DBLE on steel surface obeys Langmuir adsorption isotherm.

(2) The cathodic reductions of CRS in CH₂COOH involve hydrogen evolution, $H^+$ reaction with dissolved O₂, and the dechlorination of Cl₂CCOO⁻ . For the anodic dissolution, the adsorption of Cl₂CCOO⁻ ions on the CRS surface would be the prerequisite to occur, and both Fe²⁺ and Fe³⁺ ions are the dominant products.

(3) DBLE acts as a mixed-type inhibitor for CRS in 0.1 M Cl₂COO⁻ solution. EIS spectra exhibit a large capacitive loop at high frequencies followed by an inductive one at low frequency values. Comparing with blank solution, the presence of DBLE enhances $R_C$ while reduces $C_P$.

(4) AFM clearly shows that CRS suffers severe corrosive attack by Cl₂CCOO⁻, and the presence of DBLE could drastically retard the corrosion of steel in CCl₂COO⁻ media.

(5) MD simulations reveal that the major flavonoids in DBLE are adsorbed on Fe (001) surface through FBS with a nearby flat orientation. The sequence of either $E_{ads}$ or $E_{ads}$ is in accordance with that of inhibition efficiency: rutin > orientin > isorutin > vintin.

(6) The crude extract of DBLE exhibits better inhibition performance than the major flavonoids. Other composition compounds could have additional contribution to inhibitive performance.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work was carried out in the frame of research projects funded by the National Natural Science Foundation of China (51161023) and Training Program of Young and Middle Aged Academic and Technological Leaders in Yunnan Province (2015HB049).

References

Inhibitors

Methods


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