Short Communication

Preparation of *Isoetes sinensis* Extract as a Green Corrosion Inhibitor for Q235 Carbon Steel in Hydrochloric Acid

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Received: 10 October 2022 / Accepted: 9 November 2022 / Published: 27 December 2022

The corrosion inhibition performance of *Isoetes sinensis* extract on Q235 steel in 1 M HCl solution was investigated using polarization curves and electrochemical impedance spectroscopy. The results showed that *Isoetes sinensis* extract could significantly slow down the corrosion of carbon steel in hydrochloric acid solution. The corrosion inhibition rate reached 91% when the concentration of *Isoetes sinensis* was increased to 0.15 g/L. From the electrochemical analysis, it is clear that *Isoetes sinensis* extract mainly inhibits the cathodic corrosion reaction of carbon steel. The adsorption of corrosion inhibitor molecules in *Isoetes sinensis* extract on the carbon steel surface satisfies the Langmuir adsorption isotherm model, which is a non-homogeneous adsorption and there should be interaction forces between the adsorbed organic molecules.

**Keywords:** *Isoetes sinensis*; Corrosion inhibitor; Carbon steel; Polarization; Electrochemical impedance spectroscopy

1. INTRODUCTION

Metal pickling refers to the use of a certain concentration of acid solution to remove oxidation, rust and dirt from the metal surface. It is a pre-treatment or intermediate treatment for processes such as metal storage, painting, and rolling [1,2]. In addition, in industrial production, equipment such as boilers, heat transfer, and cooling vessels are prone to scale or rust formation on the inner surface of the equipment after long-term use, and acid cleaning is also an effective method for removing dirt from the inner walls of pipes [3]. In industry, commonly used pickling agents are generally H₂SO₄, HCl, H₃PO₄, HNO₃, H₂CrO₄, HF and mixed acids, among which sulfuric acid and hydrochloric acid are most commonly used [4–6]. However, due to the strong corrosiveness of acid, pickling removes rust and dirt, but also makes some metal substrates corroded and causes the phenomenon of "hydrogen embrittlement", resulting in the loss of metal materials (especially carbon steel materials) [7,8]. Currently, one of the most widely used and effective metal pickling protection methods in industry is
the addition of corrosion inhibitors for use. In the pickling process, adding a sufficient amount of corrosion inhibitor can form a protective film against corrosion on the metal surface [9,10]. However, the corrosion inhibitor is not adsorbed on the surface of the metal oxide, so it does not affect the dissolution of the oxide[11,12].

The commonly used metal pickling corrosion inhibitors in industry are inorganic salts such as chromates, phosphates, molybdates, and organic compounds containing P, O, N, S, π, aromatic and heterocyclic rings [13,14]. Although such corrosion inhibitors have high efficiency, but in the process of use shows many disadvantages such as toxic, high dosage and harmful to the environment. Therefore, the development of new high-efficiency, low or non-toxic environmentally friendly corrosion inhibitors instead of inorganic and organic metal corrosion inhibitors has become an inevitable trend in the development of corrosion inhibitors [15]. In recent years, researchers have focused on the research area of using green, non-toxic, low-cost and widely available substances such as plant extracts, pharmaceutical by-products, amino acids and natural polymers as corrosion inhibitors [16–18]. Among them, research on plant extracts corrosion inhibitors has attracted much attention because of their high efficiency, abundant and cheap sources, biodegradability and richness in natural chemicals [19].

A wide variety of plant extracts are used as corrosion inhibitors [20]. Studies have shown that the variety of substances in the corrosion inhibitors extracted from plants varies significantly depending on their origin, resulting in a wide range of mechanisms and types of action. Therefore, it is not possible to classify them in a uniform way to reflect the relationship between the corrosion inhibitors of different plant sources and their corrosion inhibition mechanisms [21,22]. Corrosion inhibitors extracted from plants are complex in composition and are mostly natural organic compounds or polymers containing O, N, π, aromatic and heterocyclic rings that are low or non-toxic and easily biodegradable [23]. A large number of research data show that the mechanism of corrosion inhibition of these substances mainly relies on molecular adsorption to form a molecularly oriented protective film on the metal surface, thereby inhibiting the corrosion of metals by corrosive media [24].

Due to the heterogeneity of the metal material, the nature of corrosion and corrosion inhibition in corrosive media are electrochemical in nature [25]. Therefore, the study of corrosion inhibitor corrosion inhibition mechanism and metal corrosion reaction through electrochemical methods is of great significance for the application of corrosion inhibitors in practical operation. Among the electrochemical methods, the dynamic potential polarization curve and electrochemical impedance spectroscopy are the most commonly used methods for measuring corrosion of metals. *Isoetes sinensis* is rich in chemical components such as pectin-like natural polymers. These components contain functional groups with corrosion inhibiting effects, such as -COOH, -OH, and aromatic heterocycles. Therefore, it is feasible and practical to use *Isoetes sinensis* to prepare environmentally friendly corrosion inhibitors.

2. EXPERIMENTAL

2.1. Reagents and instruments

*Isoetes sinensis* was collected from the waters around the Chongqing Institute of Engineering. The composition of Q235 carbon steel is (mass %): C 0.17, Si 0.46, Mn 0.0047, S 0.17, P 0.0047, the
rest Fe. Petroleum ether (60-90°C), 95% ethanol and concentrated hydrochloric acid were purchased from Sinopharm. The CHI660C electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd.) and the PARSTAT 2273 (Princeton Instruments, USA) electrochemical test system were used for electrochemical testing. Infrared spectroscopy (FTIR) tests were performed using a TENSOR 27 infrared spectrometer to analyze the composition of the adsorbed film layer on the surface of the steel specimens.

2.2. Preparation of Isoetes sinensis extract

The active ingredients in *Isoetes sinensis* were extracted by Soxhlet extraction method. An amount of *Isoetes sinensis* was taken and crushed with a small grinder. Add 150 mL of 95% ethanol to the round bottom flask, heat, and soxhlet extract for 8 h. Evaporate the solvent under reduced pressure. Add an appropriate amount of 1.0 M hydrochloric acid and remove the insoluble material by filtration under reduced pressure. Degreased with petroleum ether and evaporated under reduced pressure to brownish yellow oily liquid. Add 1.0 M hydrochloric acid to a 150 mL volumetric flask and set aside. Mass concentration of *Isoetes sinensis* extract = mass of *Isoetes sinensis* / volume of HCl (g/mL)

2.3. Electrochemical experiments

For electrochemical testing, Q235 carbon steel was machined into a 1 cm diameter cylinder as the working electrode. The working area is 0.785 cm² and the non-working surface is coated with epoxy resin. During the test, the electrodes were polished to a bright finish with 200#, 400#, 600#, 800# and 1200# metallographic sandpaper, scrubbed with ethanol and acetone, and cleaned with distilled water.

The electrochemical workstation and the integrated electrochemical test system were used for the dynamic potential polarization curve test and the electrochemical impedance spectroscopy test, respectively. A three-electrode system was used, with the auxiliary electrode (counter electrode) being a platinum electrode, the reference electrode being a saturated glycerol electrode, and the working electrode being a prepared Q235 carbon steel. The prepared carbon steel electrode was immersed in the 1 M HCl solution to be tested for 30 min, and the concentration of *Isoetes sinensis* extract was measured by weight (g/L). After the open circuit corrosion potential was stabilized, the polarization curves and electrochemical impedance spectroscopy experiments were carried out. The polarization curves of kinetic potential were scanned at a rate of 0.05 mV/s, and the polarization range was -1.2 to 0.5 V (vs. OCP). The electrochemical impedance spectroscopy test was performed in the frequency range of 0.01 Hz to 100 kHz, with an open circuit potential and an amplitude of 5 mV.

3. RESULTS AND DISCUSSION

As can be seen in Figure 1, the FTIR spectra of *Isoetes sinensis* and its adsorbed film on the surface of the steel sheet are very similar. The peaks at 584~615 cm⁻¹ are the O-H out-of-plane bending vibrations on the aromatic ring. The peaks at 1028~1048 cm⁻¹ are the C-O stretching perturbations on
the phenolic group [26]. The peaks at 1252 cm\(^{-1}\) correspond to the C-O-C stretching vibration of flavonoids. The broad peak at 3381 cm\(^{-1}\) belongs to the O-H stretching vibration of the glycoside molecule [27]. These characteristic peaks further confirmed the presence of flavonoids, saponins and polysaccharides in the adsorbed membrane of *Isoetes sinensis* on the steel surface [28].

![FTIR spectra](image)

**Figure 1.** FTIR spectra of the *Isoetes sinensis* extract and its adsorption film on Q235 steel.

As shown in Figure 2, the corrosion rate of the steel sheet decreased significantly after *Isoetes sinensis* was added to the hydrochloric acid solution. The corrosion inhibition efficiency increased gradually with the increase of *Isoetes sinensis* concentration. The corrosion rate of Q235 steel in blank HCl was 19.83 g·m\(^{-2}\)/h. When the concentration of *Isoetes sinensis* was increased to 0.15 g/L, the corrosion rate decreased to 1.122 g·m\(^{-2}\)/h and the corrosion inhibition efficiency reached 92.4%. This indicates that *Isoetes sinensis* has an excellent corrosion inhibition effect on Q235 steel in HCl [29]. Its adsorption coverage on the steel surface increases with the increase of *Isoetes sinensis*.

![Graph](image)

**Figure 2.** The effect of *Isoetes sinensis* extract to corrosion rate and inhibition efficiency in 1 M HCl.

Figure 3 shows the kinetic potential polarization curves of carbon steel in different concentrations of *Isoetes sinensis* extract at 25 °C. The electrochemical parameters obtained by extrapolation are shown in Table 1, where the corrosion inhibition efficiency \(\eta\) is calculated as:
\[ \eta = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100\% \]

From Figure 3 and Table 1, it can be seen that the self-corrosion potential of the electrode in *Isoetes sinensis* extract solution showed a positive shift and the corrosion current density decreased compared with that of the carbon steel electrode in the blank hydrochloric acid solution. This indicates the corrosion of carbon steel is inhibited in *Isoetes sinensis* extract solution, and with the increase of *Isoetes sinensis* extract solution concentration [30,31]. The corrosion current density decreases and the corrosion inhibition efficiency increases along with the positive shift of the self-corrosion potential. When the concentration of *Isoetes sinensis* extract was 0.16 g/L, the corrosion inhibition efficiency of carbon steel reached 91.41%.

The data in Table 1 were analyzed to calculate the anodic action coefficient \( f_a \) and cathodic action coefficient \( f_c \) for the carbon steel electrode in *Isoetes sinensis* extracts. From the results, the anodic and cathodic coefficients \( f_a \) and \( f_c \) of *Isoetes sinensis* extracts at the same concentration were very similar. The ratio of the two is approximately equal to 1, suggesting the anodic and cathodic reactions are equally inhibited for carbon steel [32]. Therefore, *Isoetes sinensis* extract is a typical mixed inhibitor corrosion inhibitor for carbon steel in HCl, and the mechanism of action is geometric coverage effect [33]. The explanation for the *Isoetes sinensis* extract being a mixed inhibition corrosion inhibitor can also be obtained from the Tafel slope in Table 1. The variations of both cathodic Tafel slope and anodic Tafel slope were not significant, indicating that *Isoetes sinensis* extract is a mixed inhibitor corrosion inhibitor [34]. Moreover, the anodic action coefficient \( f_a \) and cathodic action coefficient \( f_c \) of *Isoetes sinensis* extracts on carbon steel in HCl decreased with increasing concentration. This indicates the inhibition of the electrode reaction increases along with the inhibitor increases.

*Isoetes sinensis* contains a variety of chemical components such as polyphenols, flavonoids, caffeine, polysaccharides and amino acids. These active ingredients contain active groups such as amino, hydroxyl and carbonyl groups. These active ingredients were extracted when *Isoetes sinensis* was extracted by ethanolic infusion method [35]. On the one hand, these groups contain heteroatoms such as N and O which are electronegative. These atoms contain lone pairs of electrons and can provide electrons to the inner empty d-orbitals of the Fe atoms on the carbon steel surface [36]. They are coordinated with Fe atoms and adsorbed on the surface, thus reducing the reactivity of Fe atoms on the surface of carbon steel. In addition, because the amino and hydroxyl groups can accept H\(^+\) to form cations, they are adsorbed in the cathodic region due to the electrostatic effect, which prevents H\(^+\) from being reduced and acts as a corrosion inhibitor [37]. It can be seen that *Isoetes sinensis* extract can inhibit both cathodic and anodic reactions of carbon steel in HCl solution [38].
Figure 3. Polarization curves of Q235 in 1 M HCl with 0.01 g/L, 0.02 g/L, 0.04 g/L, 0.06 g/L, 0.10 g/L and 0.15 g/L of *Isoetes sinensis* extract at room temperature.

**Table 1.** Electrochemical parameters on Q235 in 1 M HCl with different concentration of *Isoetes sinensis* extract at room temperature.

<table>
<thead>
<tr>
<th>ρ (g/L)</th>
<th>E$_\text{corr}$ (V)</th>
<th>10$^3$ I$_\text{corr}$ (A/cm$^2$)</th>
<th>β$\text{a}$ (mV)</th>
<th>β$\text{c}$ (mV)</th>
<th>f$\text{a}$</th>
<th>f$\text{c}$</th>
<th>η (%)</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-0.457</td>
<td>0.388</td>
<td>13.031</td>
<td>13.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>-0.442</td>
<td>0.222</td>
<td>11.422</td>
<td>11.422</td>
<td>0.572</td>
<td>0.572</td>
<td>42.75</td>
<td>0.4275</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.433</td>
<td>0.145</td>
<td>10.468</td>
<td>10.471</td>
<td>0.375</td>
<td>0.375</td>
<td>61.42</td>
<td>0.6241</td>
</tr>
<tr>
<td>0.04</td>
<td>-0.426</td>
<td>0.119</td>
<td>11.288</td>
<td>11.298</td>
<td>0.308</td>
<td>0.307</td>
<td>69.76</td>
<td>0.6907</td>
</tr>
<tr>
<td>0.06</td>
<td>-0.424</td>
<td>0.080</td>
<td>10.901</td>
<td>10.901</td>
<td>0.207</td>
<td>0.207</td>
<td>78.88</td>
<td>0.7918</td>
</tr>
<tr>
<td>0.10</td>
<td>-0.420</td>
<td>0.050</td>
<td>14.662</td>
<td>14.671</td>
<td>0.117</td>
<td>0.118</td>
<td>85.85</td>
<td>0.8693</td>
</tr>
<tr>
<td>0.15</td>
<td>-0.419</td>
<td>0.033</td>
<td>13.481</td>
<td>13.481</td>
<td>0.086</td>
<td>0.086</td>
<td>91.41</td>
<td>0.9079</td>
</tr>
</tbody>
</table>

Figure 4 shows the Nyquist plots (experimental and fitted values) of Q235 in 1 M HCl solution at different concentrations of *Isoetes sinensis* extract. As seen in Figure 4, the spectral characteristics show a single time constant of the semicircular capacitive resistance arc, with the increase in corrosion inhibitor concentration. The impedance value of the electrode surface gradually increases, indicating that the corrosion rate slows down. This electrochemical system is a typical metal corrosion system in acid [39]. The impedance data can be fitted to the equivalent circuit shown in Figure 4. The electrochemical impedance parameters fitted with Zsimpwin software are shown in Table 2. The corrosion inhibition efficiency η in Table 2 is calculated as:

$$
\eta = \frac{R_p - R_{p,0}}{R_p} \times 100\%
$$
As shown in Table 2, with the increase of *Isoetes sinensis* extract concentration, the polarization resistance $R_p$ and corrosion inhibition efficiency increased, and the resistance of the electrode reaction increased. At the same time, the interfacial capacitance $C_{dl}$ of the electrode gradually decreases, indicating the adsorption of corrosion inhibitor molecules on the metal surface [40]. The maximum corrosion inhibition efficiency was up to 91.12%, which was in good agreement with the polarization curve data. The solution resistance $R_s$ remains almost unchanged due to the adsorption reaction. The active ingredient in the corrosion inhibitor molecule blocks the water molecules adsorbed on the surface of the Q235. The corrosion inhibitor forms an adsorption layer on the surface of Q235. In addition, because the dielectric constant of adsorbed water molecules is larger than the dielectric constant of *Isoetes sinensis* extract [41], the capacitance of the interfacial layer formed by the corrosion inhibitor adsorbed on the surface of Q235 is smaller than the capacitance of the interfacial layer formed by water molecules and the surface of Q235 [42]. A comparison of inhibition performance has been supplied in Table 3.

**Table 2.** EIS parameters of Q235 in 1 M HCl with different concentration of *Isoetes sinensis* extract at room temperature.

<table>
<thead>
<tr>
<th>$\rho$ (g/L)</th>
<th>$R_s$ (Ω/cm$^2$)</th>
<th>$10^6$ $C_{dl}$ (F)</th>
<th>$n$</th>
<th>$R_p$ (Ω/cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.23</td>
<td>528.8</td>
<td>0.8616</td>
<td>22.3</td>
<td>53.15</td>
</tr>
<tr>
<td>0.01</td>
<td>1.77</td>
<td>567.8</td>
<td>0.7833</td>
<td>48.8</td>
<td>71.26</td>
</tr>
<tr>
<td>0.02</td>
<td>2.35</td>
<td>487.9</td>
<td>0.7741</td>
<td>81.7</td>
<td>77.71</td>
</tr>
<tr>
<td>0.04</td>
<td>1.78</td>
<td>515.7</td>
<td>0.7355</td>
<td>102.6</td>
<td>77.71</td>
</tr>
<tr>
<td>0.06</td>
<td>2.09</td>
<td>504.6</td>
<td>0.7548</td>
<td>125.9</td>
<td>78.38</td>
</tr>
<tr>
<td>0.10</td>
<td>2.11</td>
<td>424.6</td>
<td>0.7312</td>
<td>213.6</td>
<td>88.08</td>
</tr>
<tr>
<td>0.15</td>
<td>1.20</td>
<td>424.7</td>
<td>0.7395</td>
<td>255.3</td>
<td>91.12</td>
</tr>
</tbody>
</table>
Table 3. Comparison of inhibition efficiency of Isoetes sinensis extract with reported data of previous inhibitors.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>c (inhibitor)</th>
<th>ηw (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ginkgo leaf</td>
<td>0.8 g/L</td>
<td>77.7</td>
<td>[43]</td>
</tr>
<tr>
<td>Spinacia oleracea</td>
<td>500 ppm</td>
<td>92.4</td>
<td>[44]</td>
</tr>
<tr>
<td>Betel nut shell</td>
<td>0.5 g/L</td>
<td>93.1</td>
<td>[45]</td>
</tr>
<tr>
<td>Eupatorium Adenophora</td>
<td>0.1 g/L</td>
<td>91.3</td>
<td>[46]</td>
</tr>
<tr>
<td>Isoetes sinensis</td>
<td>0.15 g/L</td>
<td>91.12</td>
<td>This work</td>
</tr>
</tbody>
</table>

In order to further investigate the adsorption behavior of the effective corrosion inhibiting components of Isoetes sinensis extract on the surface of Q235, the results of the polarization curve test were fitted to the adsorption isotherm equation, and the results showed that the adsorption of Isoetes sinensis extract on the surface of Q235 was in accordance with the Langmuir isotherm equation:

$$\frac{\theta}{1-\theta} = K\rho$$

where ρ is the mass concentration of the added Isoetes sinensis extract (g/L), θ is the surface coverage, θ = η (see Table 1), and K is the adsorption equilibrium constant. Plotting ρ against θ/(1 - θ), the fitting results are shown in Figure 5, which indicates that its adsorption on the surface of Q235 belongs to monomolecular layer adsorption.

![Figure 5](image)

Figure 5. Langmuir adsorption isotherms for Isoetes sinensis extract on Q235 in 1 M HCl.

4. CONCLUSION

Corrosion inhibitor from Isoetes sinensis was extracted by Soxhlet extraction method and showed some corrosion inhibition on Q235 in 1 M HCl. The corrosion inhibition efficiency increased with the increase of the extract concentration. When the concentration of Isoetes sinensis extract was 0.15 g/L, it showed a good corrosion inhibition effect on carbon steel. The electrochemical test results showed that Isoetes sinensis extract was a mixed inhibitor type corrosion inhibitor and the mechanism of action was
geometric coverage effect. The adsorption of the effective corrosion inhibiting components on the carbon steel surface was monolayer adsorption and satisfied the Langmuir adsorption isotherm.

References

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