

Study on the Extract of *Raphanus Sativus L* as Green Corrosion Inhibitor for Q235 Steel in HCl Solution

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In this work, the extract of *Raphanus sativus L* (Sinapine thiocyanate, Inhi-ST) as green inhibitor was extracted and isolated by the dried and powdered semen raphanin from *Raphanus sativus L*. After the target green inhibitor isolated, it was characterized by ESI-MS, ¹H and ¹³C-NMR. Meanwhile, the corrosion inhibition of Q235 steel (QS) by Inhi-ST in HCl solution was evaluated using weight loss and potentiodynamic polarization measurement. The study results indicate that Inhi-ST is an effective green corrosion inhibitor for QS corrosion in HCl solution, the green corrosion inhibitor is a mixed-type inhibitor, and the inhibition efficiency increase with Inhi-ST concentration increasing, while which decrease with HCl concentration, temperature and storage time increasing. In addition, the adsorption of Inhi-ST on QS follows Langmuir isotherm, which is the mixed adsorption involving both chemisorption and physisorption.

Keywords: Semen Raphanin; Green Inhibitor; Electrochemical; Weight Loss; Chemisorption.

1. INTRODUCTION

Use of inhibitor is one of the simple methods to protect different metals against corrosion under the acidic medium for cleaning, chemical decaling and pickling. During the past decade, a number of organic compounds have been reported as effective corrosion inhibitor [1-4]. Due to the toxicity of some synthetic organic corrosion inhibitors, there has been increasing search for green corrosion

inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Many investigations have been reported using such naturally occurring substances as green corrosion inhibitor for several metals in different media. For example, Hassan [5] reported that the *Citrus aurantium* leave extracts can act as a sustainable corrosion inhibitor for mild steel (MS) in H₂SO₄ solution, and the effect of temperature, time and leave extracts concentration on inhibition efficiency were presented. And the studies reported by Umoren [6] and Bhawsar [7] show that the *Sida acuta* leaves and stem extracts, and the *Nicotiana tabacum* extract also can act as the green inhibitor for MS in H₂SO₄ solution. Meanwhile, Al-Otaibi [8] investigated that some extracts including *Anvillea garcinii* extracts, *Tripleurospermum auriculatum*, *Lycium shawii*, *Ochradenus baccatus*, *Artemisia sieberi*, *Teucrium oliverianum*, *Cassia italic* and *Carthamus tinctorius* extracts all can act as the effective green corrosion inhibitor for MS in acidic media. In addition, the influence of natural occurring extract of *Chenopodium ambrosioides* on the corrosion inhibition of carbon steel in H₂SO₄ solution was studied by Bammou [9]. According to the study reported by Eduok [10], the synergistic action caused by KI on the corrosion inhibition of MS in H₂SO₄ solution by leaves and stem extracts of *Sida acuta* was presented. Based on the study by Obi-Egbedi [11], *Spondias mombin L.* as a green corrosion inhibitor for aluminium in H₂SO₄ solution was studied. In addition, the effect of *Tinospora crispa* and *Ficus hispida* leaves extracts as the green inhibitors for MS corrosion inhibitor in HCl solution were reported by Hussin [12] and Znini [13], respectively.

Although several extracts from plant as green corrosion inhibitors have been reported, however, there are few reports about the extract of *Raphanus sativus L.* as green corrosion inhibitor. *Raphanus sativus L.*, considered to be an economically important perennial aquatic crop, has been cultivated all over China. The dried ripe seed of *Raphanus sativus L.*, also called *Semen Raphani*, were primarily used to help digestion, eliminate distension and reduce phlegm. *Sinapine thiocyanate* was obtained from *Semen Raphani* and modern pharmaceutical studies showed that compound possessed various biological activities, including antihypertensive, treat constipation and alleviate chronic tracheitis.

In the present study, the aim of this work is to develop the new effective green corrosion inhibitor and investigate the corrosion inhibition of Q235 steel (QS) in HCl solution by the extract of *Raphanus sativus L.*

2. MATERIALS AND METHODS

2.1 Materials

In this work, all the used reagents and solvents containing hydrochloric acid (HCl, 37%), potassium thiocyanate (KSCN), methanol (MeOH), ethanol (EtOH), petroleum ether and ethyl acetate were analytical grade (A.R.) and purchased from Kelong Inc. (Chengdu, China). The *Semen Raphani* was purchased from Lotus Pond Chinese Herbal Medicine Market in Chengdu, Sichuan Province of China, in September 2017. A voucher specimen (20170917) was deposited in our laboratory.

NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz for ¹H and 100

MHz for ^{13}C), with chemical shift (δ) values given in ppm and TMS as internal standard. Low resolution ESI-MS were measured on a Finnigan LCQ^{DECA} ion-trap mass spectrometer (San Jose, CA, USA); RP-C₁₈ (Welch). Precoated silica gel GF₂₅₄ (10-40 μm) plates for TLC and silica gel (100-200 mesh and 200-300 mesh) for column chromatography (CC) were purchased from Qingdao Haiyang Chemical Company (Qingdao, China). Spots were visualized under UV light at 254 nm and by spraying with Drogen-droff reagent.

CHI 660D electrochemical workstation was used to record Tafel polarization curve. All the rectangle test specimens (5 mm×20 mm×50 mm) and working electrode were prepared by QS. The potentiodynamic polarization (Tafel) measurement was conducted by a counter Pt electrode, a saturated calomel reference electrode (SCE) and the QS working electrode. In addition, during the whole testing process, temperature was controlled by HH-1 water thermostat (China). The various concentrations of HCl solutions were prepared by hydrochloric acid (HCl, 37%) and deionized water.

2.2 Extraction and isolation

The dried and powdered semen Raphani (50.0 kg) were extracted with EtOH at 50°C three times (100 L, 2d, each) and evaporated under reduced pressure to yield a dark brown crude extract (8.5 kg). The crude extract was suspended in 90% MeOH and extracted with petroleum ether (3×3 L). After concentrating the 90% MeOH layer in vacuo, the residue (1.5 kg) was suspended in water and then extracted with ethyl acetate. The water layer fraction (1.2 kg) was subjected to silica gel column chromatography (25×120 cm, 100-200 mesh, 4kg) using ethyl acetate/methanol (100:0 ~0:100) as gradient system to give fractions 1-5. Fraction 5 (112.0 g) was applied to an RP-C₁₈ column (10×55 cm, 600 g), eluting with MeOH/H₂O (10:90) to afford fractions 2a-2c. Fraction 2b (70.0 g) was mixing in 500 mL of 0.1 mM KSCN water solution and standing at 5°C until solid powder precipitate in the bottom of the flask. Further purification of the solid powder was achieved by recrystallization with methanol, yielded Sinapine thiocyanate (Inhi-ST, 35.3 g), namely 2-[(E)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoyl]oxyethyl-trimethyl-azanium thiocyanate, showing in figure 1.

2.3 Weight loss and electrochemical measurement

Weight loss measurement as the classical method for corrosion inhibition studying, this method was described in literatures [14-16]. According to this method, the corrosion rate (v) and the corresponding inhibition efficiency ($IE_{\text{Wt}}(\%)$) were calculated from Eq. (1) and (2). In this work, m_1 and m_2 are the mass of the QS specimen before and after corrosion, S is the total surface area of the QS specimen, t is the immersion time, v_0 and v are corrosion rate of the QS specimen corrosion in HCl solution in without and with different concentrations of Inhi-ST.

$$v = (m_1 - m_2) / St \quad (1)$$

$$IE_{\text{Wt}}(\%) = 100\% \times (v_0 - v) / v_0 \quad (2)$$

Potentiodynamic polarization (Tafel) measurement as an important method to study the corrosion inhibition of Inhi-ST in HCl solution was conducted by conventional three-electrode system,

and all potential in this study were referred to SCE. The potential sweep rate for this measurement to obtain the Tafel curves was 0.5 mV s^{-1} . The corresponding inhibition efficiency ($IE_{\text{Tafel}} (\%)$) was calculated as Eq. (3) [17-19]. In this equation, i_{corr} and $i_{\text{corr}(i)}$ are the corrosion current density for QS corrosion in HCl solution in the absence and presence of different concentration of Inhi-ST.

$$IE_{\text{Tafel}} (\%) = 100\% \times (i_{\text{corr}} - i_{\text{corr}(i)}) / i_{\text{cor}} \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Spectroscopic data of Inhi-ST

White amorphous powder (MeOH); ESI-MS m/z : 310 ($[M]^+$) $^1\text{H-NMR}$ (400 MHz, MeOH) δ : 7.67 (1H, d, $J = 16.0 \text{ Hz}$, H-7), 6.94 (2H, s, $J = 16.0 \text{ Hz}$, H-8), 4.66 (2H, m, H-10), 3.88 (6H, s, -O-CH₃), 3.80 (2H, m, H-11), 3.27 (9H, s, -N-CH₃). $^{13}\text{C-NMR}$ (100 MHz, MeOH) δ : 166.4 (C-9), 148.5 (C-3, 5), 146.7 (C-7), 139.1 (C-4), 130.0 (C \equiv N), 124.7 (C-1), 114.6 (C-8), 106.9 (C-2, 6), 64.7 (C-1'), 58.6 (C-2'), 56.6 (3, 5-OCH₃), 53.5 (N-CH₃).

3.2. Structural elucidation

Inhi-ST, a white amorphous powder, has been proved to be alkaloids by Dragon-droff reagent color-reaction. The molecular formula was established as C₁₆H₂₄NO₅CNS by ESI-MS at m/z 310 $[M]^+$ and NMR data. The UV spectrum exhibited absorption maxima at 232 and 328 nm. In the $^1\text{H-NMR}$ spectrum, the characteristic trans-double bond signals at δ_{H} 7.67 (1H, d, $J = 16 \text{ Hz}$) and 6.94 (1H, d, $J = 16 \text{ Hz}$) were observed, together with a pair of symmetric aromatic ring signals at δ_{H} 6.94 (2H, s), two O-methyl signals at δ_{H} 3.88 (6H, s), three N-methyl signals at δ_{H} 3.27 (9H, s) and two pairs of methylene signals at δ_{H} 4.66 (2H, m) and 3.80 (2H, m). The existence of an ester carbonyl carbon (δ_{C} 166.4) and a cyano carbon (δ_{C} 130.0) were revealed from the $^{13}\text{C-NMR}$ spectrum. Based on the above evidences and compared with the known compounds, the compound was determined to be Sinapine thiocyanate (2-[(E)-3-(4-hydroxy-3,5-dimethoxy-phenyl)prop-2-enoyl]oxyethyl-trimethyl-azanium thiocyanate, Inhi-ST).

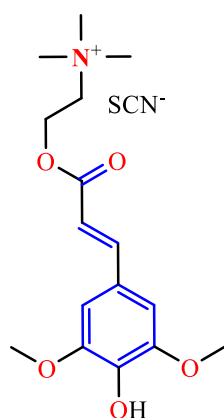


Figure 1. Chemical structure of Sinapine thiocyanate (Inhi-ST).

3.3 Potentiodynamic polarization measurement

All the polarization curves for QS corrosion in 1.0 M HCl with various concentrations of Inhi-ST at 30°C obtained from potentiodynamic polarization measurement were presented in figure 2. According to the polarization curves, all the electrochemical parameters containing i_{corr} (corrosion current density), E_{corr} (corrosion potential), b_c (cathodic Tafel slopes), b_a (anodic Tafel slopes) and $IE_{\text{Tafel}}(\%)$ (corresponding inhibition efficiency) were listed in table 1.

Based on the polarization curves (see figure 2) and electrochemical parameter (in table 1), which reveals that the i_{corr} decrease with adding Inhi-ST in 1.0 M HCl. On the other hand, the i_{corr} decrease with Inhi-ST concentration increasing indicates that the inhibition effect enhances with the increase of Inhi-ST concentration. The inhibition process is attributed to the formation of an adsorbed film of the extract of *Raphanus Sativus L* as green inhibitor on QS surface which protects QS against corrosion in HCl solution. The possible mechanism is the adsorption of the green inhibitor on QS surface through the electron pair of heteroatoms (N, O, S) and the conjugated systems (benzene rings, C=C, C=O) in molecular of Inhi-ST showing in figure 1. Obviously, the formed Inhi-ST film can block QS corrosive in HCl solution.

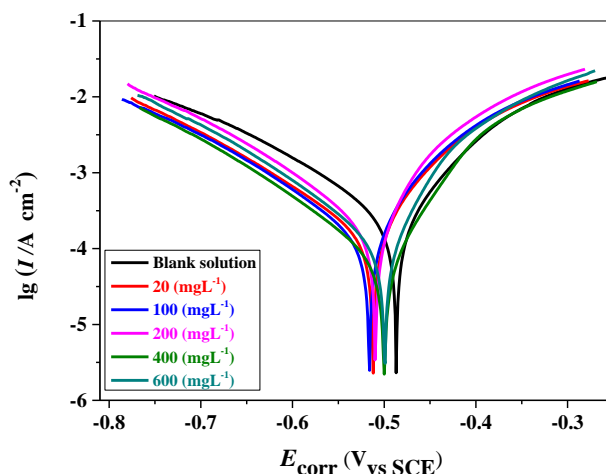


Figure 2. The polarization curves of QS corrosion in 1.0 M HCl in the absence and presence of various concentrations of Inhi-ST at 30°C.

Table 1. The electrochemical parameters of QS corrosion in 1.0 M HCl in the absence and presence of various concentrations of Inhi-ST at 30°C.

c (mgL^{-1})	E_{corr} (V)	i_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV dec^{-1})	b_c (mV dec^{-1})	IE_{Tafel} (%)
0	-0.487	1438.6	93.8	155.5	-
20	-0.512	331.8	98.5	128.0	76.9
100	-0.516	273.8	99.2	122.2	81.0
200	-0.510	239.6	106.6	120.1	83.3
400	-0.500	178.9	99.5	116.6	87.6
600	-0.499	101.8	72.4	117.5	92.9

Furthermore, according to table 1, it is obvious that the i_{corr} is much smaller in the presence of Inhi-ST comparing with that in the absence of Inhi-ST for QS corrosion in 1.0 M HCl, and which decreases with Inhi-ST concentration increasing. With the Inhi-ST concentration increase from 20 to 600 mg L⁻¹, the IE_{Tafel} are increased from 76.9% to 92.9%, this result reveal that Inhi-ST can act as effective green corrosion inhibitor for QS in HCl solution.

Additionally, according to Tafel measurement, the green corrosion inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the HCl blank solution [20-21]. Based on Tafel curves showing in figure 2 and the electrochemical parameters listing in table 1, it can be found that the corrosion potentials shift slightly in the negative direction. All corrosion potential of QS in 1.0 M HCl with Inhi-ST at 30°C shifts less than 25 mV, which indicates that Inhi-ST as the extract of *Raphanus Sativus L* is a mixed-type green corrosion inhibitor.

3.4 Weight loss measurement

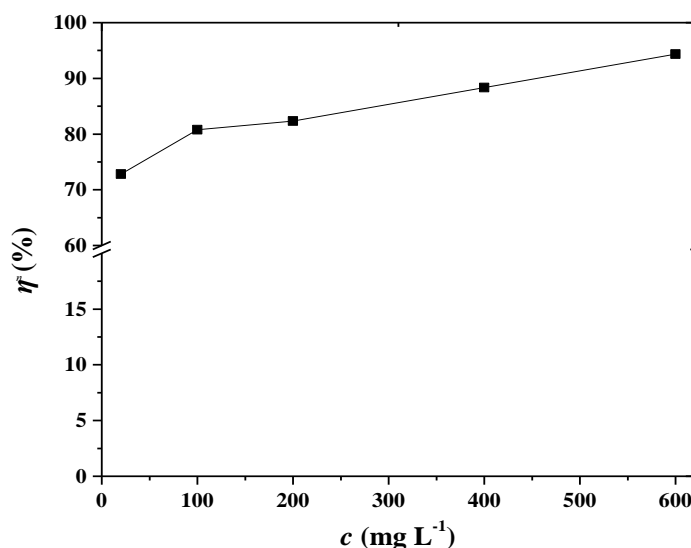


Figure 3. The effect of Inhi-ST concentration on $IE_{\text{Wt.}}$ (%) for QS in 1.0 M HCl at 30 °C.

Based on weight loss measurement, the variation in inhibition efficiency ($IE_{\text{Wt.}}$ (%)) with concentration of the green corrosion inhibitor for QS in 1.0 M HCl at 30°C was exhibited in figure 3. From this figure, it can be seen clearly that the $IE_{\text{Wt.}}$ is found to increase with the concentration of Inhi-ST, when the Inhi-ST concentration increase from 20 to 400 mg L⁻¹, the $IE_{\text{Wt.}}$ change slightly with inhibitor concentration further increase. The increase in $IE_{\text{Wt.}}$ is due to the increase in the number of constituent molecules of Inhi-ST adsorbed on the QS surface at higher concentration, so that the active sites of the QS are protected by the green inhibitor molecules. With Inhi-ST concentration increase to 600 mg L⁻¹, the $IE_{\text{Wt.}}$ reaches 94.36%. This result is in good agreement with the result obtained from Tafel measurement.

3.5 Adsorption isotherm

It is well known that the adsorption isotherms can provide basic and important information on the interaction between the green inhibitor of Inhi-ST and QS surface. Usually, both the physisorption and chemisorption as two main types of interaction are used to describe the adsorption of inhibitor on metals surface. From the result of weight loss method showing in figure 3, in order to confirm the reasonable adsorption isotherm for Inhi-ST on QS surface in HCl solution, various isotherms (Langmuir and Temkin adsorption isotherms, etc.) are employed using the data of weight loss measurement. Fitting results reveal that the adsorption of Inhi-ST on QS surface obey Langmuir adsorption isotherm, showing in Eq. (4) [22-24]. In this equation, c is the concentration of Inhi-ST, θ is the fractional surface coverage, K is the adsorption equilibrium constant. θ for various concentrations of Inhi-ST in 1.0 M HCl is calculated using Eq. (5).

$$c/\theta = 1/K+c \tag{4}$$

$$\theta = (v_0-v)/v_0 \tag{5}$$

The plots of c/θ versus c yield the straight lines shown in figure 4. And the strong correlation ($R^2=0.99613$, see figure 4) shows that Inhi-ST adsorption on QS surface in 1.0 M HCl obey Langmuir adsorption isotherm. Meanwhile, the ΔG (standard free energy of adsorption) is calculated from Eq. (6), where $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T=303 \text{ K}$.

$$K = \exp(-\Delta G/RT) \times 1/55.5 \tag{6}$$

According to Eq. (6), the calculated values of ΔG for Inhi-ST corrosion in 1.0 M HCl at 30°C is $-34.89 \text{ kJ mol}^{-1}$, which higher than $-40.00 \text{ kJ mol}^{-1}$ and lower than $-20.00 \text{ kJ mol}^{-1}$. The result also indicates that the adsorption processes of Inhi-ST on QS surface in HCl belongs to mixed adsorption, which involve both physisorption and chemisorption [14, 19, 23, 25].

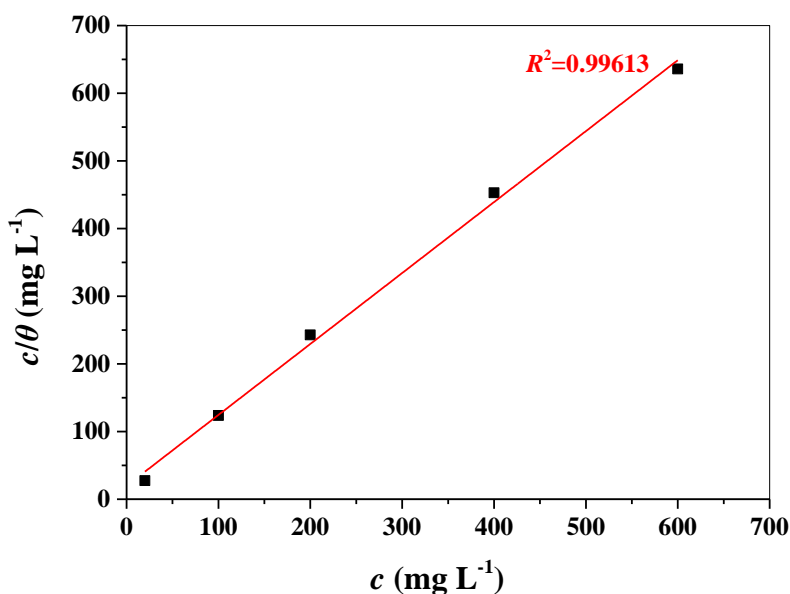


Figure 4. Langmuir adsorption isotherm for Inhi-ST on QS in 1.0 M HCl at 30°C.

3.6 Effect of temperature, HCl concentration and storage time on inhibition efficiency

The effect of temperature (T , °C) on corresponding inhibition efficiency ($IE_{Wt.}(\%)$) obtained by weight loss measurement was presented in figure 5. From this figure, it can be found that the $IE_{Wt.}$ decrease with temperature increasing, with temperature increase from 25°C to 45°C that the $IE_{Wt.}$ drop from 97.2% to 90.2% for QS in 1.0 M HCl with 600 mg L⁻¹ Inhi-ST. The decrease of $IE_{Wt.}$ is due to the increase of the temperature might cause desorption of the green inhibitor constituents from QS surface, and the decrease in the strength of adsorption process at higher temperatures. Compare the mild steel inhibitor of pyrazolo carbothioamide derivative of (E)-4-(2-(4-methoxy phenol)hydrazono)-3-methyl-5-oxo-4,5-dihydro-1H-pyrazole-1-carbothioamide [26], 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane [27] and extracts of *Sida acuta* [10] with the green inhibitor of Inhi-ST in this work, it is clearly that the effect of temperature on $IE_{Wt.}$ have a same influence tendency.

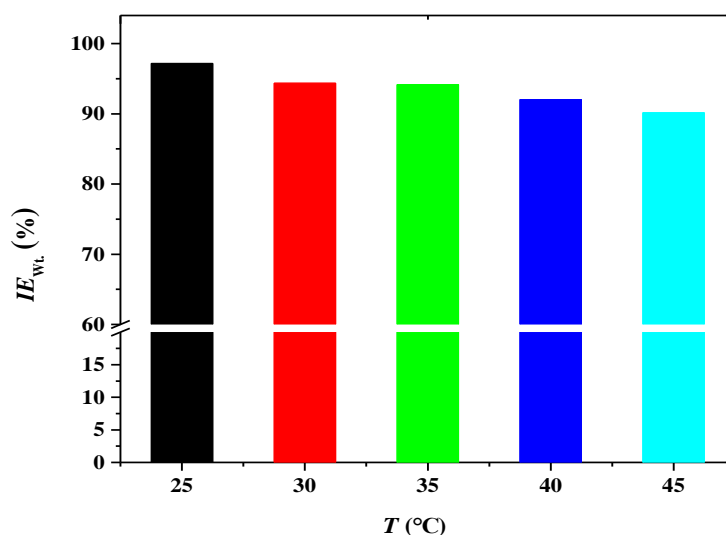


Figure 5. The effect of temperature on $IE_{Wt.}(\%)$ for QS in 1.0 M HCl with 600 mg L⁻¹ Inhi-ST.

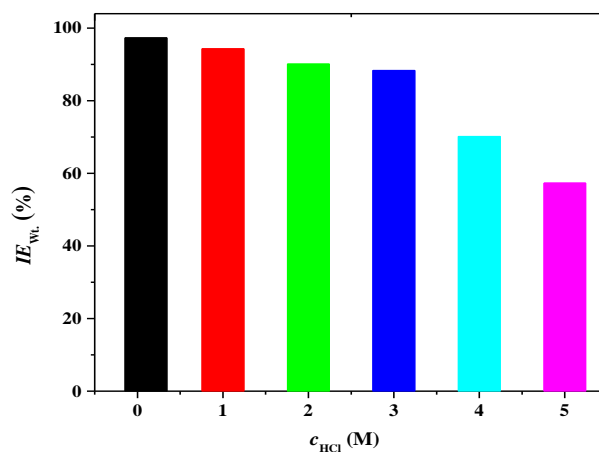


Figure 6. The effect of HCl concentration on $IE_{Wt.}(\%)$ for QS in 1.0 M HCl with 600 mg L⁻¹ at 30°C.

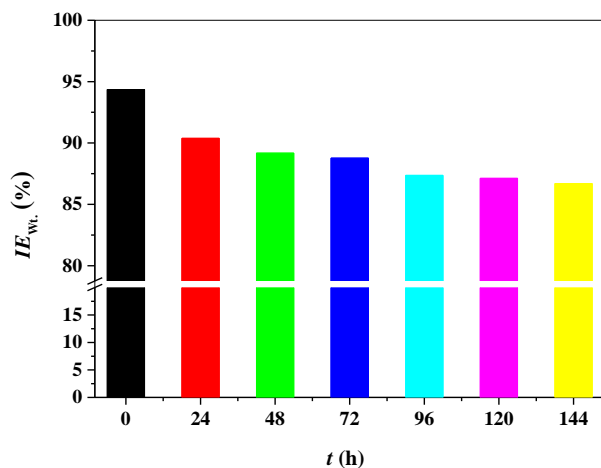


Figure 7. The effect of storage time on IE_{Wt} (%) for QS in 1.0 M HCl with 600 mg L⁻¹ Inhi-ST at 30°C.

The effect of HCl concentration (c_{HCl} , M) on IE_{Wt} at 30°C was shown in figure 6. From this figure, it is obvious that IE_{Wt} decrease with HCl concentration increasing, the IE_{Wt} of QS corrosion in 0.1 M and 5.0 M HCl with 600 mg L⁻¹ Inhi-ST are 97.3% and 57.3%, respectively. The decrease of IE_{Wt} by increase of HCl concentration is contributed to the increase of hydrogen ion concentration in HCl solution. And the similar result was reported by Gou [28].

In 1.0 M HCl with 600 mg L⁻¹ Inhi-ST at 30°C, the effect of storage time on IE_{Wt} was presented in figure 7, it can be found that the IE_{Wt} decrease with storage time increasing, which is decreased significantly, especially in 24 hours. After added this inhibitor in 1.0 M HCl at 24 hours and 144 hours, the inhibition efficiency decreased from 94.4% to 86.7%, respectively. We concluded that the decrease of IE_{Wt} is due to the hydrolysis of the extract of *Raphanus Sativus L* (Inhi-ST, Sinapine Thiocyanate) in acid solution showing in figure 8. Obviously, although the inhibitor of Inhi-ST was hydrolyzed in 24 hours, the hydrolysis products also exhibited the excellent corrosion inhibition. This is due to the fact that the IE_{Wt} remains as high as 86.7% after the hydrolysis of 24 hours.

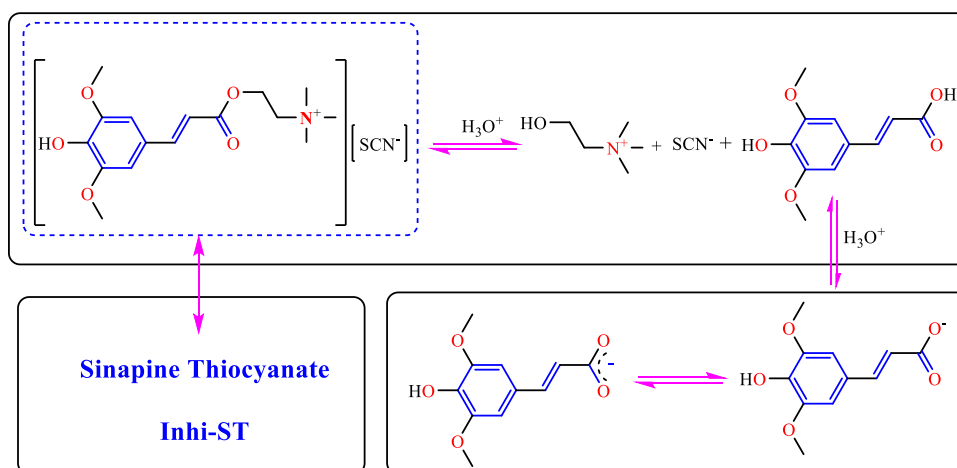


Figure 8. The hydrolysis of the Inhi-ST in acid solution.

4. CONCLUSIONS

In conclusion, the green inhibitor of Sinapine Thiocyanate (Inhi-ST) was extracted and isolated by the dried and powdered semen raphanin from *Raphanus Sativus L.* After the target green inhibitor extracted and isolated, it was confirmed by ¹H-NMR, ¹³C-NMR and ESI-MS. Meanwhile, the corrosion inhibition of Q235 steel (QS) by Inhi-ST in HCl solution was evaluated using weight loss and potentiodynamic polarization measurement. The study results indicate that the Inhi-ST as the extract of *Raphanus Sativus L.* is an excellent eco-friendly green inhibitor. The green inhibitor of Inhi-ST is a mixed-type inhibitor. The inhibition efficiency increase with Inhi-ST concentration increasing, decrease with HCl concentration, temperature and storage time increasing. The adsorption of Inhi-ST on QS surface was found to obey Langmuir's adsorption isotherm. Meanwhile, the standard free energy of adsorption indicated that the adsorption of Inhi-ST on QS surface belongs to mixed adsorption which involving both chemisorption and physisorption.

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