Study of Eco-Friendly Corrosion Inhibition for Mild Steel in Acidic Environment

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Abstract

The inhibition effect of Chamaemelum Nobile extract on corrosion of mild steel electrode in 1.0 molar hydrochloric acid was studied using gravimetric analysis and electrochemical methods. Results from the experimental studies have shown that, as the inhibitor concentration increases the inhibition efficiency. The adsorption of the inhibitor molecules on mild steel surface obeys Langmuir adsorption isotherm. Scanning electron microscope performed a surface study with and without inhibitors for mild steel. From all the results in this research, we found that Chamaemelum Nobile extract was an attractive alternative to prevent corrosion as it shows the great inhibition efficiency.

Keywords: Corrosion inhibition, CNE, Mild steel and hydrochloric acid.

1. Introduction

Corrosion inhibitors are the chemical compounds that able to inhibit the oxidation process of metal in aqueous media and consequently inhibit the corrosion processes [1-3]. Mild steel is important metal which used in different human activities and it is susceptible to different mechanisms of corrosion due to its exposure to different corrosive acidic media. Hydrochloric acid is usually used as industrial acid cleaning and pickling acids, but it affects negatively on the metal surface due to containing aggressive ion (Cl-) [4]. The corrosion inhibitors should be added in small doses without effects on the metal surface[4]. According to various research works, the corrosion inhibitors include organic, inorganic and surfactants compounds[5].

Organic substances with heterocyclic atoms (N, O, and S) have been used as excellent inhibitors but these organic substances difficult to prepare and cost have toxic effects on humans [6-9] Such toxic affections by the use of the organic inhibitors have led to the use of natural products as corrosion inhibitor for mild steel in acidic media, which are safe and harmless from the environment [10-16]. Green corrosion inhibitors especially plant parts play a very important role in corrosion protection due they are biodegradable, easily available and can be extracted by simple procedures with low cost [5]. Chamomiles flower is an official drug (recognized by government authority) in the pharmacopoeia of 26 countries. At present this plant is known as one of the main medicinal herbs and is listed in major pharmacopoeia such as British Pharmacopoeia. Chamomile is known to be anti-inflammatory, Anti-allergic antispasmodic and anti-bacterial activities. The essential oil and flower extracts contain about more than 120 secondary metabolites[17-19].The existence of some organic compounds in the Chamaemelum Nobile extract (CNE) containing a variety of heterogeneous oxygen atoms, aromatic rings, unsaturated carbonyl compounds and (hydroxyl and methyl) groups, render them excellent inhibitors of corrosion[20]. Janmejai group[21] examined the pharmacological properties of aqueous and methanolic fraction isolated from chamomile. HPLC-MS analysis of chamomile extract confirmed apigenin-7-O-glucoside as the major constituent of chamomile.

The aim of the present work is to study the corrosion inhibition properties of the O-glucoside extracted from CNE in 1.0 M hydrochloric acid at various concentrations are to investigate for Mild steel electrode using Wight loss, various
electrochemical methods as well as SEM analysis. We hope that the present work will assist design new and effective corrosion inhibitors in the future. The most noteworthy inhibition efficiency was affirmed by scanning electron microscopy.

2.2. EXPERIMENTAL SECTION

2.1. Materials Preparation.

Tests were performed on mild steel specimens with weight percentage composition as follows: C 0.17, Si 0.022, Mn 0.71, P 0.010, Cr 0.045, Ni 0.072, Al 0.0017, Cu 0.182, Sn 0.011, F 0.022, Mo 0.011, and Fe 98.74. The inhibitor extracted according to Janmejai group[21]. A 1.0 mol. L⁻¹ HCl solution is prepared from a 37 % concentrated solution were purchased from Al-Gomhoria Company, Egypt and used as a corrosive medium. The inhibitor used herein at concentrations of 1 to 5 g/l was prepared in 1.0 M hydrochloric acid solutions at 30 °C. The natural product used in this study is shown in Figure 1.

Fig. 1 Chamaemelum Nobile Extract CNE

2.2. Non Electrochemical Measurements[22]

Weight loss measurements were conducted on test coupons of dimensions 5cm×1cm×0.1cm. Before immersion the obvious electrodes in the test solution each of them are prepared by polishing with emery paper from 1000 to 1400 grade to obtain a smooth surface, washing with distilled water and then decreased with acetone about 5 minutes, washed again with distilled water then dried it by used filter papers. A sample of tested metal, previously carefully degreased and polished is weighed and immersed in an electrolyte solution for specified time (t). After that time, the sample is taken out, sluiced, degreased, and weighted. The average weight loss (ΔW) is calculated by following equation (1)

\[
\Delta W = W_1 - W_2 \quad (1)
\]

Where \( W_1 \) and \( W_2 \) is samples weight before and after immersion in electrolyte solution for t time, respectively. ΔW is represented in grams. Based on obtained results, corrosion rate can be estimated as

\[
C. R = K \times \Delta W / A \times t \times d \quad (2)
\]

Where \( K \) is a constant \( (8.76 \times 10^6) \) which allows representing C,R in mm/year; \( A \) is the surface of the metal sample (cm²); \( t \) is the immersion time (hours), \( d \) is the density of the metal (g/cm³). The inhibition efficiency (% IE) and degree of surface coverage (θ) of CNE acting as inhibitor in 1.0 M HCl was calculated using the following expression (3):

\[
\theta = IE /100 = [(C. R_{blank} - C. R_{inhibitor}) / C. R_{blank}] \quad (3)
\]

2.3. Electrochemical measurements

The electrochemical behaviour of the mild steel sample in 1.0 mol.L⁻¹ HCl solution at various concentrations of the CNE abrasion-resistant at 30 °C was researched applying open circuit potential (OCP) for 30 min to an equilibrium state was achieved. Potentiodynamic polarization tests were performed to estimate corrosion device Tafel slopes using the EG&G potentiostat/galvanostat version 273A with corrosion analysis software 352/252 2.01 (Princeton Applied Research, USA). The linear polarization (LP) was calculated from –20 to +20 mV versus \( E_{corr} \). The Tafel plots (TP) were traced from –250 to +250 mV versus \( E_{corr} \). The scanning rates for LP and TP calculating were 0.166 and 0.4 mV/S, correspondingly [23]. In the existence and non-existence of the CNE-inhibitor, electrochemical impedance spectroscopy (EIS) was utilized to examine the attitude of mild steel after 2 h of inundation. A sinusoidal signal voltage of 10 mV was operated in a frequency limit of \( 10^3 \) to \( 10^5 \) Hz. EIS measurements were performed with an AUTO AC DSP device (ACM Instruments) device. All impedance analyses were done at the open circuit potential and 30 °C [23, 24].

2.4. Scanning electron microscope (SEM)

A scanning electron microscope (SEM) is employed to investigate the exterior-surface morphology and topology of mild steel when the inhibitor is present and absent. SEM was assessed using JEOL (JEOL Ltd, Tokyo, (Japan) JSM 5400 LV Scanning Microscope (Assiut University electron microscopy unit).

3. Results and Discussion

3.1. Weight loss measurements

The corrosion rate of the mild steel in the without and with of CNE at room temperature was studied using weight loss technique. Table 1 show the calculated values of corrosion rate (mmpy), inhibition efficiency and the degree of surface coverage for mild steel dissolution in 1.0 M HCl in the absence and presence of the CNE, which indicated their ability to inhibit the corrosion of mild steel in 1.0 M HCl solutions. This effect is attributed to increase of the surface coverage of the metal surface by inhibitor molecules when the inhibitor concentration is
increased. Increasing the surface coverage by inhibitor molecules decreases the contact between the metal surface and the aggressive medium that also decreases the corrosion effect of that medium on the metal. It also showed that there is a direct proportional relationship between the inhibitor concentration and both corrosion inhibition efficiency and period of experiment figure 2.

3.2. Electrochemical measurements

3.2.1. Open circuit potential

Fig. 3 illustrates the variation of the open circuit potential of the mild steel electrode was submerged for 30 min in blank solution as well as in the existence of concentrations of inhibitor at (30 °C) to establish steady-state open circuit potential. After measuring the steady state open circuit potential for blank solution shifts to slightly negative potential than values of immersion potential, that indicates the destruction of pre-immersion oxide film on the electrode surface[25].

When different concentrations of CNE are added as an inhibitor to the aggressive medium, values of steady-state open circuit potential shift towards positive direction of potential than the steady state open circuit potential of blank, due to formation an layer of CNE molecules on the mild steel surface which effect directly on the anodic corrosion reaction[26].

3.2.2. Polarization measurements

The anodic and cathodic polarization curves was documented for the mild steel corrosion in absence and presence of CNE concentration 1 to 5 g/l in blank solution at as exhibited in Figure 4, the data of Polarization, such as abrasion potential ($E_{\text{corr}}$), (C.R), inhibition efficiency polarization ($\eta_{p\%}$) and coverage surfaces ($\theta$) are obtained from Tafel polarization curve extrapolation. These parameters can be found in Table 2. The CR, $\eta_{p\%}$ and ($\theta$) are calculated from equations (3, 4)

\[
C.R = \frac{0.13 \times E_{\text{corr}} \times (\text{Eq.Wt})}{A \times d}
\]

Where Eq.wt. Is the metal equivalent mass, A is the area ($\text{cm}^2$), d is density ($\text{g/cm}^3$) and 0.13 is time conversion factor.

The gained results in Table 2 exhibited that the C.R of mild steel in the deficiency of CNE abrasion-resistant increased steeply whereas the C.R increases slowly in the present concentrations of CNE as inhibitor[27]. The corrosion-repression efficiency values rise in the presence of CNE inhibitor and protective action can be assigned to the electron density; this electron density differs with the substituents in the inhibitor molecules. Table 2

<table>
<thead>
<tr>
<th>Time immersion (hrs.)</th>
<th>Conc. Of inhibitors (g/L)</th>
<th>$\Delta W$ (g)</th>
<th>CR (mmpy)</th>
<th>IE (%)</th>
<th>Surface coverage ($\theta$)</th>
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</thead>
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<tr>
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<td>21.313</td>
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</tr>
<tr>
<td></td>
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<td>0.0888</td>
<td>20.645</td>
<td>31.429</td>
<td>0.314</td>
</tr>
</tbody>
</table>

Table 1. Wight loss parameters of CNE on the corrosion of mild steel in 1.0 M HCl at 30°C
slowly in the present concentrations of CNE as inhibitor[27]. The corrosion-repression efficiency values rise in the presence of CNE inhibitor and protective action can be assigned to the electron density; this electron density differs with the substituents in the inhibitor molecules. Table 2

Fig. 2 Variation of inhibition efficiency with CNE concentration and immersion time in 1.0 M HCl at room temperature.

Fig. 3 Potential-time curves for mild steel in 1.0 M HCl at different concentrations of inhibitors after 1day exposure time at 30°C.

The active centers in the molecule that carbonyl groups interact with the mild steel surface via electron donation to the empty d-orbital of iron thereby enabling the adsorption of the CNE molecule to the mild steel surface

3.2.3. Electrochemical impedance spectroscopy

Impedance parameters such as charge-transfer resistance \((Rct)\), The double-layer capacitance \((Cdl)\), \(\theta\) and inhibition efficiency impedance \((\eta.I \%)\) for the mild steel corrosion after 1 day exposure time at 30°C in the absence and presence of different CNE concentrations in 1.0 M HCl solution shown in Table 3.

The \((Cdl)\), the \((\eta.I \%)\) and \(\theta\) were calculated from the following equations (5, 6)[28, 29]:

\[
\text{Cdl} = \frac{1}{2\pi f_{\text{max}}R_{\text{ct}}} = \frac{1}{2\pi f_{\text{max}}R_{\text{ct}}} (6)
\]

Where:
- \(f_{\text{max}}\) = The frequence at the maximum in the Nyquist plot.
- \(R_{\text{ct}}\) = The values of charge transfer resistance.
- \(Cdl\) = double layer capacitance obtained from the Nyquist plots.

The obtained Nyquist plot for the mild steel corrosion after 1day exposure time at 30°C in the absence and presence of different concentration CNE in 1.0 M HCl solution is shown in Fig. 5
Adsorption (ΔGads) is the first step in the inhibitor action. Molecules of the natural product can adsorb in four types on the metal surface:

i) Electrostatic interaction between the charged molecules and the charged metal surface.

ii) Interaction of unshared electron pairs in the molecules and metal.

iii) Interaction of π-electrons in the metal.

iv) A combination of the type (i) and (iii).

In order to gain more information about the mode of adsorption of these natural products on the surface of mild steel, the experimental data have been tested with several adsorption isotherms, including Langmuir, Frumkin, Freundlich and Temkin isotherms. However, the best fit is obtained from the Langmuir isotherm. The correlation between surface coverage (θ) defined by (IE% /100) and the concentration of inhibitor (C) can be represented by the Langmuir adsorption isotherm, the isotherm is given by equation (7)(32).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

(7)

Where K is the adsorption constant, C is the concentration of the inhibitor and surface coverage values (θ) which obtained from the weight loss measurements for various concentrations. The correlation coefficient (R²) was used to choose the isotherm that best fit experimental data. The strong correlation (R² >0.999) suggests that the adsorption of inhibitor on the mild steel surface obeyed this isotherm. The relation between C/ θ and C is shown in Fig. 6 these plots are linear with a slope equal to unity. This suggests that the adsorption of (CNE) on metal surface followed the Langmuir adsorption isotherm. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species. The equilibrium constant for adsorption process is related to the free energy of adsorption (ΔGads) and is expressed by following equation (8)(33).

$$K_{ads} = \left(\frac{1}{55.5}\right) \exp \left(\frac{-\Delta G_{ads}}{RT}\right)$$

(8)

Where 55.5 is the molar concentration of water in the solution expressed in M (mol⁻¹), T is the absolute temperature (K) and R is the gas constant (8.314 J K⁻¹ mol⁻¹).

<table>
<thead>
<tr>
<th>Test solution</th>
<th>Conc. Of inhibitors (g/L)</th>
<th>Rct (Ω cm²)</th>
<th>Cdl (μF cm⁻²)</th>
<th>η.I (%)</th>
<th>Surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>………………</td>
<td>54</td>
<td>135.33</td>
<td>………</td>
<td>………………</td>
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<tr>
<td>CNE</td>
<td>1</td>
<td>123</td>
<td>28.59</td>
<td>56.10</td>
<td>0.561</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>159</td>
<td>15.69</td>
<td>66.04</td>
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</tr>
<tr>
<td></td>
<td>3</td>
<td>219</td>
<td>8.62</td>
<td>75.34</td>
<td>0.753</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>456</td>
<td>2.36</td>
<td>88.16</td>
<td>0.882</td>
</tr>
</tbody>
</table>

Fig. 5 Nyquist plots for mild steel in 1.0 M HCl at different concentrations of inhibitors after 1day exposure time at 30°C and Equivalent circuit used to fit the impedance data.

The diameters of the capacitive loop obtained increases in the presence of CNE, and were indicative of the degree of inhibition of the corrosion process[30] . EIS data in Table 3 indicating that Rct increases and Cdl decreases with the increasing of CNE inhibitor concentrations. The increase in Rct values, and consequently of η.I %, may be due to the gradual replacement of water molecules by the adsorption of the CNE molecules on the metal surface to form of film on the metal surface. And this suggests that the coverage of the metal surface by the film decreases the double layer thickness. Also, this decrease of Cdl at the metal/solution interface with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicates that the inhibitors were adsorbed on the surface at both anodic and cathodic sites[31].

The equivalent circuit for mild steel after 1-day exposure time at 30°C in 1.0 M HCl in the with and without of different concentrations of CNE is shown in Fig. 5.

3.3. Adsorption Isotherm

It is a general assumption that, at the metal interface, the adsorption of the natural product inhibitors is the first step in the inhibitor action mechanism.

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Equation (8) can be modification into equation (9) for calculating ΔG_{ads} as follow:

\[ ΔG_{ads} = -2.303RT\log (55.5K) \]  

(9)

ΔG_{ads} of (CNE) for mild steel in 1.0 M HCl at different exposure times (24, 48, 72 and 96 hrs.) were calculated using the slope and the ordinate axis intercept of the straight lines. The deducted values were summarized in Table 4.

Table 4. Values of Langmuir adsorption parameters at exposed mild steel to different CNE in 1.0 M HCl.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Immersion time (hrs.)</th>
<th>Slope ( \bar{R} )</th>
<th>( R^2 )</th>
<th>ΔG_{ads, kJ mol^{-1}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNE</td>
<td>24</td>
<td>0.83</td>
<td>0.95</td>
<td>-9.58</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>1.06</td>
<td>0.99</td>
<td>-9.42</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>1.41</td>
<td>0.99</td>
<td>-8.55</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>2.78</td>
<td>0.99</td>
<td>-8.36</td>
</tr>
</tbody>
</table>

Fig. 6 Curves fitting of CNE adsorption by Langmuir isotherm for mild steel in 1.0 M HCl. Generally, values ΔG_{ads} are ranged from -8.36 to -9.58 kJ mol^{-1}. Values ΔG_{ads} in the order -20 kJ mol^{-1} or lower indicate the electrostatic interaction between organic charged molecules and the charged metal. In other words, these values indicating that natural products (CNE) are physically adsorbed on the metal surface, while those around -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to from a co-ordinate type of bond (chemisorption)[35]. The large negative values of ΔG_{ads} indicate that the adsorption reaction proceeds spontaneously and is accompanied by highly efficient adsorption.

3.4. Scanning electron microscope

Fig. (7A) illustrates the surface morphology of polished mild steel electrode before exposure to corrosion media. The micrograph is shown in the Fig. (7B) show polished specimen which was kept in the blank solution of (1.0 M HCl), at 1 day, shows an aggressive attack of the corroding medium on the steel surface. Fig. (7C) shows specimen which was kept in (1.0 M HCl) in the presence of at 5 gm/l of CNE as inhibitor after 1 day exposure time at 30°C, suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes the corrosion rate of metal appreciably.

Fig. 7 SEM image of mild steel surface after 1 day immersed in 1.0 mol. L^{-1} HCl at room temperature (A) polished mild steel (B) in absence and (C) in existence of 5 g/l of CNE-inhibitor.

4. Conclusions

- The experimental results obtained show that CNE act as effective inhibitors of mild steel corrosion in 1.0 M HCl. The compound with maximum inhibition activity is (89.4 %).
- It is seen that inhibition efficiency values of the CNE as inhibitor increases with increasing concentration.
- The adsorption of the CNE on mild steel surface from 1.0 M HCl is a physical phenomenon proposed from the values of obtained and obeys Langmuir adsorption isotherm.

5. Reference

STUDY OF ECO-FRIENDLY CORROSION INHIBITION FOR MILD STEEL IN …


Arabic Abstract

تمت دراسة تأثير التثبيط على تآكل قطع الصلب الخفيف في حمض الهيدروكلوريك 0.1 مولار باستخدام تحليل الوزن النوعي والطرق الكهروكيميائية. أظهرت نتائج الدراسات التجريبية أن تركيز المثبط يزيد من كفاءة التثبيط. يتمتص امتصاص جزيئات المثبط على سطح الصلب الخفيف باستخدام إلامتوير. أجرى المجهر الإلكتروني الماسح دراسة سطحية عن ودائع الصلب الخفيف. ومن جميع النتائج في هذا البحث وجدنا أن Chamaemelum Nobile extract إن بديلاً جذابًا لمنع التآكل لأنه يظهر كفاءة التثبيط.