Ингибитирование коррозии мягкой стали экстрактами листьев Custard apple и Acacia concinna в кислой среде: адсорбционное и термодинамическое исследование

Джитендрра Кисан Шинде, Равиндра Гулаб Пури, Паван Девидас Мешрам, Раджкумар Шанкаррао Сирсам

Экстракт листьев Custard apple (CALE) был протестирован для оценки эффективности ингибитирования коррозии мягкой стали в кислой среде. Исследуемый металлический субстрат собирали в течение 24 ч после контакта с кислотой для определения эффективности ингибитирования коррозии (CIE) и скорости коррозии (CR) с использованием гравиметрического анализа. Результаты исследования были применены для изучения адсорбционного поведения и термодинамических характеристик CALE как потенциального ингибитора коррозии в кислой среде. Мягкая сталь показала самую высокую скорость коррозии в отсутствие ингибитора коррозии в 0,5 М растворе серной кислоты. Однако наблюдалось постепенное снижение скорости коррозии с увеличением концентрации CALE (0,4–2,0 г/л). Аналогичная тенденция отмечена в экспериментальном интервале температур 298–328 К. Поведение адсорбции исследовали с использованием моделей изотерм адсорбции Ленгмюра, Темкина, Фрейндлиха и Флори Хаггинса. Модель изотермы адсорбции Темкина лучшим образом соответствует экспериментальным данным. Кроме того, отрицательные значения свободной энергии адсорбции Гиббса (ΔG_ad) убедительно свидетельствуют о спонтанном характере адсорбции CALE на поверхности мягкой стали. Увеличение энергии активации (E_a) от 35,05 кДж/моль в холостом растворе до 68,03 кДж/моль при концентрации CALE 2,0 г/л свидетельствует об образовании защитной пленки из молекул ингибитора на поверхности металла. Значения энтропии адсорбции (ΔS) в диапазоне концентраций (0–2,0 г/л CALE) подразумевают физическую адсорбцию, тогда как отрицательные значения энтропии (ΔS) предполагают свободное движение молекул ингибитора в объеме раствора. Кроме того, был продемонстрирован синергетический эффект в снижении скорости коррозии при сочетании экстракта Acacia concinna (ACE, 0,1–0,3 г/л) с CALE, повышающий общую эффективность ингибирования коррозии.

Ключевые слова: листья Custard apple, Acacia concinna, гравиметрический анализ, ингибитирование коррозии, мягкая сталь

Для цитирования: Джитендрра Кисан Шинде, Равиндра Гулаб Пури, Паван Девидас Мешрам, Раджкумар Шанкаррао Сирсам Ингибитирование коррозии мягкой стали экстрактами листьев Custard apple и Acacia concinna в кислой среде: адсорбционное и термодинамическое исследование. Изв. вузов. Химия и хим. технология. 2024. Т. 67. Вып. 7. С. 119–126. DOI: 10.6060/ivkkt.20246707.7038.

CORROSION INHIBITION BEHAVIOUR OF CUSTARD APPLE LEAVES AND ACACIA CONCINNA EXTRACT ON MILD STEEL IN ACIDIC MEDIA: ADSORPTION AND THERMODYNAMIC STUDY

Jitendra Kisan Shinde, Ravindra Gulab Puri, Pawan Devidas Meshram, Rajkumar Shankarrao Sirsam

Custard apple leaves extract (CALE) was tested to evaluate corrosion inhibition efficiency for mild steel under acidic medium. The test metal substrate was collected over a period of 24 hr of contacting with acid to determine the corrosion inhibition efficiency (CIE) and corrosion rate (CR) using the Gravimetric analysis. The findings of the study were applied to examine the adsorption behavior and thermodynamic characteristics for CALE as a potential corrosion inhibitor in acidic environment. Mild steel exhibited the highest corrosion rate in the absence of a corrosion inhibitor in a 0.5 M sulphuric acid solution. However, the rate of corrosion was observed to decrease gradually with increase in CALE concentration (0.4–2.0 g/l). The similar trend was noted at the experimental temperature range of 298–328 K. Adsorption behavior was investigated using the Langmuir, Temkin, Freundlich, and Flory Huggins adsorption isotherm models. The Temkin adsorption isotherm model provides the best fit to the experimental data. Besides, the negative values of Gibb’s free energy of adsorption (ΔGad) reveal strong evidence for the spontaneous nature of CALE adsorption on mild steel surface. The increase in activation energy (Ea) from 35.05 kJ/mol in the blank test solution to 68.03 kJ/mol at 2.0 g/l concentration of CALE indicates the formation of a protective film of inhibitor molecules on the metal surface. Adsorption enthalpy values (∆H=31.28–73.79 kJ/mol) over the concentration range (0-2.0 g/l of CALE) implies physical adsorption, whereas negative entropy values (∆S) suggests free movement of inhibitor molecules in the bulk solution. Additionally, a synergistic effect was demonstrated in lowering the corrosion rate by combining Acacia concinna extract (ACE, 0.1-0.3 g/l) with CALE, thereby enhancing the overall corrosion inhibition efficiency.

Key words: Custard apple leaves, Acacia concinna, gravimetric analysis, corrosion inhibition, mild steel

INTRODUCTION

Equipments in the chemical as well as metal industries are continuously exposed to alkalis, acids, and different corrosive fluids [1]. This drew the attention of global researchers to minimize corrosion of materials of construction of various equipments. Various organic and inorganic corrosion inhibitors have been studied by researchers to resolve the issue [2-3]. The theory of corrosion inhibition assumes that the inhibitor molecules diffuses from the bulk of the solution and
become adsorbed on the metal surface, forming a protective thin layer that provides mass transfer resistance against reactive species from the bulk of the solution to the solid-liquid interface. Hetero-atoms from organic inhibitor and inorganic inhibitors based on heavy metals demonstrated significant corrosion inhibition efficiency [4-8]. The majority of these inhibitors are expensive and harmful to both human and environment. This imposed the search of new corrosion inhibitors that are affordable, eco-friendly, and effective.

Previous research has demonstrated the application of bio-based products as corrosion inhibitors, including fruits, seeds, leaves, roots, and extract from plants. These naturally occurring corrosion inhibitors have been presented as alternative to synthetic inhibitors and are frequently employed as corrosion inhibitors because they are inexpensive, readily available and biodegradable in nature [1, 9]. Several researchers have worked on extracts obtained from solid waste products as corrosion inhibitors, in- cluding fruits, seeds, leaves, roots, and extract from Haematostaphis barteri [10], Rhus verniciflua [11], Argemone Mexicana [12], Rothmannia longiflora [13], Acacia catechu [14], Luffa cylindrica [15], Citrus aurantiifolia [16], Haematostaphis barteri [17], Ficus tikoua [18], Ficusb leaves [19], Pterocarpus santalinoides [20], Morinda Tinctoria [21], and Borassus flabellifer coir dust [22]. Natural compounds such as polysaccharides and high molecular surfactants have also been employed extensively as corrosion inhibitors, since they significantly reduce the rate of corrosion [9, 23]. Certain functional groups of surfactants, which can either anodic or cathodic, have an ability to adsorb on the metal surface and create stronger linkages [2, 24]. Such type of characteristic bonding forms more protective film on the surface and provides greater resistance to corrosion compared to the conventional inhibitor [24].

In the present study, alcoholic extract of Custard apple leaves was used to investigate its corrosion inhibition behavior in 0.5 M sulphuric acid on mild steel. The standard adsorption isotherms were used to evaluate the corrosion mechanism, and the thermodynamic parameters of adsorption were determined. Moreover, the combined effect of Acacia concinna extract (ACE) with Custard apple leaves extract (CALE) was studied.

**MATERIALS AND METHODS**

**Custard apple leaves extract and electrolyte solution preparation**

Custard apple leaves from local area was collected and washed several times with water to remove dust and then air dried at 40 °C for 5 h. The dried leaves were subjected to Soxhlet extraction with ethanol (1:3 w/v) for 4 h. The extraction process yields a blackish-green liquid designated as Custard apple leaves extract (CALE), used as a stock solution for corrosion inhibition studies. 0.5 M sulphuric acid solution was prepared as corrosive media.

**Metal substrate preparation**

Standard grade mild steel (Fe-99.33%, Mn-0.44%, Cu-0.06%, P-0.17%) strips were polished sequentially with Emery paper of various grades 400-2000. The strips were then degreased with ethanol, acetone and finally washed with distilled water.

**Gravimetric studies**

Mild steel strips (5 cm × 4 cm × 0.5 cm) were weighed and immersed for 24 h in 0.5 M sulphuric acid solution to study its corrosive effect on the metal surface. The experiments were performed with and without CALE as corrosion inhibitor at different concentrations in acidic media. The identical experiments were carried with 0.1 g/l CALE concentration at 298 K in presence of ACE at different concentrations under otherwise similar conditions. At the end of experiments, metal strips were removed from the test solution, washed with double-distilled water, dried and polished with Emery paper to remove corrosion product formed over the metal surface. Final weight of the strips was recorded, and corrosion rate (CR), corrosion inhibition efficiency (CIE) and surface coverage (θ) was determined using Equation (1), (2) and (3) respectively.

\[
CR \text{(mmpy)} = \frac{∆W×87600}{DAt}
\]

where \( ∆W \) = change in weight (gm), \( A \) = area of the sample exposed (cm²), \( D \) = density of mild steel (7.86 gm/cm³) and \( t \) = exposed time (h).

\[
CIE \, (\%) = \frac{W_{wo}-W_w}{W_{wo}} \times 100
\]

where \( W_{wo} \) = change in weight without inhibitor (gm), \( W_w \) = change in weight with inhibitor concentration (gm).

\[
θ = \frac{R_o-R_i}{R_o}
\]

where \( R_o \) and \( R_i \) are the corrosion rate with and without inhibitor.

**RESULT AND DISCUSSION**

**Corrosion rate (CR) and Corrosion inhibition efficiency (CIE)**

The effect of variation in CALE concentration across a temperature range of 298 to 328 K on CR and CIE is presented in Fig. 1. It has been noted that CR decreased and CIE increased as CALE concentration increased at all working temperatures. The change in CR was relatively higher at elevated temperature of 328 K than at lower temperatures 298, 308 K. This might be the result of increased kinetic energy of the interacting CALE molecules as temperature rises [25]. Increased CALE concentration augmented CIE, which
at higher temperatures resulted in a considerable decline in CIE. This could be due to decline in resistance offered by adsorbed inhibitor molecules on the metal surface as the temperature rises [26-27].

Besides, this study also examined the feasibility and nature of adsorption by evaluating the change in Gibb’s free energy of adsorption (ΔG_{ad}) at different temperatures.

\[ \Delta G_{ad} = -RT \ln (55.5K_{ad}) \]  

where \( R \) is the gas constant (8.314 J/mol.K), \( T \) is the absolute temperature, and the value 55.5 is the concentration of water in solution expressed in M.

The ΔG_{ad} values at all tested temperatures are negative (Table 1) indicate that the adsorption of CALE molecules onto steel surface is spontaneous process. Typically, values of ΔG_{ad} up to −20 kJ/mol are consistent with the electrostatic interaction (physical adsorption), whereas values more than −40 kJ/mol involves formation of coordinate covalent bonds (chemisorption). The calculated ΔG_{ad} values at each temperature are much lower than 20 kJ/mol, which is indicative of physical adsorption mechanism for CALE molecules to adhere on the surface of mild steel.

### Adsorption Isotherms

The corrosion protection approach involves the surface coverage through adsorption of inhibitor molecules on the metal surface. Hence, the nature of interaction between CALE and the mild steel surface was investigated using several adsorption isotherms such as Langmuir, Temkin, Freundlich and Flory Huggins models. The best fit isotherm to identify the adsorption process was thus explained by utilizing the values of the surface coverage (\( \theta \)) at various CALE concentrations in acid media in the temperature range of 298–328 K. The isotherms were constructed to determine the surface coverage (\( \theta \)) according to following equations:

**Langmuir:**
\[ \frac{CR}{\theta} = \frac{1}{K_{ad}} + CR \]  

**Temkin:**
\[ \theta = \log CR + K_{ad} \]  

**Freundlich:**
\[ \log \theta = \log K_{ad} + n \log CR \]  

**Flory Huggins:**
\[ \log \frac{\theta}{CR} = \log (1 - \theta) + \log K_{ad} \]

Plots of the experimental surface coverage (\( \theta \)) and corrosion rate (\( CR \)) data adopted for these isotherms at different temperatures are displayed in Fig. 2. The data was consistent with the models proposed by Langmuir, Temkin, Freundlich, and Flory Huggins.

However, based on the regression coefficients (R²) values obtained for each model, the Temkin isotherm was identified as the best fit to explain the mechanism of adsorption of CALE on metal surface in sulphuric acid media. The equilibrium constant (\( K_{ad} \)) values calculated from the Temkin plot for the studied temperature range are listed in Table 1. The positive values of \( K_{ad} \) support the feasibility of adsorption of CALE inhibitor molecules on the surface of mild steel. In addition, increase in \( K_{ad} \) values are noted for temperature rise implies that the adsorbed inhibitor molecules are removed from the metal surface and diffuses back into the bulk acid solution [27].

### Thermodynamic Study

A clear understanding of the potential mechanism of inhibitor adsorption can be gained by analyzing the temperature dependence of inhibition efficiency and comparing the corrosion activation energies in the presence and absence of inhibitor. Accordingly, the Arrhenius equation was used to calculate the apparent activation energy (\( E_a \)) for the corrosion process in both the presence and absence of the CALE inhibitor.

\[ \log CR = \frac{-E_a}{2.303RT} + \log \gamma \]  

where \( \gamma \) is Exponential factor.

### Table 1

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( K_{ad} ) (mol²)</th>
<th>( \Delta G_{ad} ) (kJ/mol)</th>
</tr>
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<tbody>
<tr>
<td>298</td>
<td>1.7529</td>
<td>-13.713</td>
</tr>
<tr>
<td>308</td>
<td>2.6313</td>
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<tr>
<td>318</td>
<td>3.0027</td>
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</tr>
<tr>
<td>328</td>
<td>4.1372</td>
<td>-10.743</td>
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</table>
The Arrhenius plot of log $CR$ against $(1/T)$ is shown in Fig. 3A for different concentration of CALE. The linearization of the plot shows consistency with experimental data ($R^2 = 0.99$). Table 2 presents the estimated values of $E_a$ for mild steel in presence of CALE (0.4 - 2.0 g/l) in acid solution. The results demonstrate that $E_a$ value rises to 40.21 kJ/mol at 0.4 g/l CALE compared to $E_a = 35.05$ kJ/mol in absence of inhibitor. This is likely that the adsorbed CALE molecules offered a physical barrier for the charge transfer among the metal substrate and acid media, resulted into lowered rate of corrosion. Also, $E_a$ values were significantly increased with increasing CALE concentration that suggests physical adsorption mechanism, where a protective layers of inhibitor molecules is formed on the metal surface, is becoming dominant. Consequently, an improved mass transfer resistance is established at higher CALE concentration in acid media that prevents reactive species diffusing from the bulk of the solution to metal surface [29-30]. In present work, the values of $E_a$ are in the range of 35.05 - 68.03 kJ/mol for CALE concentrations of 0.4-2.0 g/l. These values are relatively lower than the threshold value of 80 kJ/mol required for stronger interaction in chemisorption mechanism [31]. Therefore, it is confirmed that interaction of CALE molecules that led to adsorption on the surface of mild steel followed the physical adsorption.

An alternate representation of the Arrhenius equation in the transition state for the dissolution and adsorption process is given in Equation (10).

$$\log \frac{CR}{T} = -\Delta H \frac{1}{2.303R} \left(\frac{1}{T}\right) + \ln \left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303R}\right)$$  \hspace{1cm} (10)

where, $h$ – Planck’s constant, $Nh$ – Avogadro’s number.

The linear transition state plots of log($CR/T$) versus $(1/T)$ for the respective CALE concentrations and temperature (Fig. 3B) were used to estimate the enthalpy ($\Delta H$) and entropy ($\Delta S$) of corrosion process and are presented in Table 2. The positive values of $\Delta H$ reflect the endothermic nature of steel dissolution process. At higher CALE concentrations (1.6-2.0 g/l), the values of $E_a$ are slightly greater than corresponding values of $\Delta H$ indicates that at higher CALE concentrations corrosion process may be engaging hydrogen evolution reaction, which would result into decreased
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total reaction volume. Further, the values of $\Delta H$ obtained ranged between 31.28-73.79 kJ/mol at different concentrations of CALE are much lower than 100 kJ/mol and indicated a physical adsorption mechanism [29, 32]. The large and negative values of entropy ($\Delta S$) reveal a decrease in disorderliness, implying the free movement of CALE inhibitor molecules in the bulk acid solution prior to be adsorbed on the surface of mild steel and formed an activated iron-complex [33].

Fig. 3. Arrenius and Transition state plot for mild steel in absence and presence various concentrations of CALE: (A) Arrenius plot of log CR vs (1/T): 01-Blank, 02-0.4 g/l, 03-0.8 g/l, 04-1.2 g/l, 05-1.6 g/l, 06-2.0 g/l, (B) Transition state plot of log (CR/T) vs 1/T: 01-Blank, 02-0.4 g/l, 03-0.8 g/l, 04-1.2 g/l, 05-1.6 g/l, 06-2.0 g/l

Рис. 3. График Аррениуса и переходного состояния для мягкой стали в отсутствие и в присутствии различных концентраций CALE: (A) График Аррениуса log CR в зависимости от (1/T): 01-контрольный, 02-0,4 г/л, 03-0,8 г/л, 04-1,2 г/л, 05-1,6 г/л, 06-2,0 г/л, (B) График переходного состояния log (CR/T) в зависимости от 1/T: 01-контрольный, 02-0,4 г/л, 03-0,8 г/л, 04-1,2 г/л, 05-1,6 г/л, 06-2,0 г/л

**Table 2**

<table>
<thead>
<tr>
<th>CALE Conc. (g/l)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>35.05</td>
<td>31.28</td>
<td>-214.76</td>
</tr>
<tr>
<td>0.4</td>
<td>40.21</td>
<td>37.63</td>
<td>-217.37</td>
</tr>
<tr>
<td>0.8</td>
<td>49.51</td>
<td>46.97</td>
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</tr>
<tr>
<td>1.2</td>
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<td>1.6</td>
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</tr>
<tr>
<td>2.0</td>
<td>68.03</td>
<td>73.79</td>
<td>-228.81</td>
</tr>
</tbody>
</table>

**Effect of Acacia concinna extract (ACE)**

The cumulative effect of varying concentration of ACE with CALE (1.0 g/l) on rate of corrosion and efficiency of corrosion inhibition at 298 K is illustrated in Fig. 4. The corrosion rate ($CR$) was measured to be 13.14 mmpy with corrosion inhibition efficiency ($CIE$) of 59.48% at 0.1 g/l of ACE concentration. Nevertheless, the rate of corrosion drops to 4.05 mmpy and the inhibition efficiency rises to 89.56% at a concentration of 0.3 g/l of ACE. This significant change with increase in ACE concentration is attributed to the attachment of characteristic groups to the mild steel surface. This, in turn, creates a shield on the metal surface that improves the effectiveness of corrosion inhibition [34].

The assessment of experimental data obtained for combination of ACE and CALE on corrosion inhibition also followed Temkin adsorption isotherm ($R^2 = 0.928$). The calculated values of $K_{ad}$ and $\Delta G_{ad}$ are 1.075 mol$^{-1}$ and -18.02 J/mol respectively.

Fig. 4. Plot of CR and CIE at various ACE concentrations (CALE conc. 1.0 g/l, 298 K, 24 h): 01- CR, 02- % CIE

Рис. 4. Зависимости CR и CIE при различных концентрациях АПФ (концентрация CALE 1,0 г/л, 298 К, 24 ч): 01- CR, 02- % CIE

**CONCLUSIONS**

Extract of Custard apple leaves was found to be an effective corrosion inhibitor in 0.5 M sulphuric acid media within the temperature range studied. The adsorptive interaction of CALE molecules on the metal
surface showed physical adsorption mechanism as confirmed by the Temkin isotherm fit to the experimental data and the negative $\Delta G_{ad}$ values implies the spontaneity of the adsorption process. Further, the addition of extract of Acacia concinna with CALE showed a synergistic effectiveness in inhibiting the corrosion of mild steel. Thus, present work provides an efficient method of using ACE as surfactant material in compound with vegetal origin CALE inhibitor to prevent metal surface corrosion.

The authors declare the absence a conflict of interest warranting disclosure in this article.

References


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