Corrosion Inhibition Effect of Aerial Parts of Euphorbia Caducifolia for Aluminium in HNO₃

Reena Sharma and Alok Chaturvedi
Synthetic and Surface Science Laboratory, S.P.C. Govt College, Ajmer, Raj. India.

**ARTICLE INFO**

**Article history:**
Received: 20 January 2018; Received in revised form: 1 March 2018; Accepted: 10 March 2018;

**Keywords**
Anti Rust Solution, Corrosion Inhibitor, Euphorbia Caducifolia, Weight Loss, Thermometric.

**ABSTRACT**

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. The most common kinds of corrosion result from electrochemical reactions. It can be prevented if the metal is coated with something which does not allow moisture and oxygen to react with it. It can be controlled by either alloying or by anti rust solutions. The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitor. Euphorbia caducifolia has been selected to study its corrosion inhibition efficiency. It is easily available in any season. It is native to Thar Desert of India and located on rocky terrain, hills. It is used for treatment of bleeding wound, cutaneous eruption, urinary problems, kidney stones, rheumatic pain, bronchitis, jaundice, diabetics, stomach pain, hernia etc. It is also called “Thor” and “Danda-thor”. It contains caudicifolin) norcycloartane type triterpene, cyclocaducinol, triterpenes euphol, turcальнol and cycloartenol. Corrosion inhibition efficiency of aerial parts of Euphorbia caducifolia was studied for aluminium in HNO₃. Maximum inhibition efficiency was found 92.17% in 1N HNO₃ acid with 0.8% leaf corrosion inhibitor whereas it was 90.53% for stem and 89.94% for flower with same concentration of inhibitor i.e. 0.8%. Inhibition efficiency was studied in different concentration of acid (1N, 1.5N, 2N and 2.5N) with different concentration of inhibitor (0.2%, 0.4%, 0.6% and 0.8%). Weight loss and thermometric methods were used. Inhibition efficiency was found to be increase with increase in concentration of inhibitor and decrease with increase in acid strength.

Introduction

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. The most common kinds of corrosion result from electrochemical reactions. It affects almost all the metals and decays the metallic properties of metals. It is unavoidable process but it can be prevented if the metal is coated with something which does not allow moisture and oxygen to react with it. It can be controlled by either alloying or by using corrosion inhibitors (anti rust solution)³.

Aluminium alloys with a wide range of properties are used in engineering structures. The strength and durability of aluminium alloys vary widely, not only as a result of the components of the specific alloy, but also as a result of heat treatments and manufacturing processes. A lack of knowledge of these aspects has from time to time led to improperly designed structures and gained aluminium a bad reputation.

In the acid, oxidation of metal occurs and hydrogen gas evolved. In the environment so many harmful gases and acids are present in the air which disintegrate and degrade the metal and alloy by corrosion. In industries acids are widely used in many processes so we need to use corrosion inhibitors which prevent or decrease the loss of metal.

A number of N and S containing ligands have been synthesized ⁴-⁵ which are found as effective corrosion inhibitors. Some heterocyclic compounds and their derivatives have been also used for metals as corrosion inhibitors in acidic media ⁶-⁹. Epoxy esters inhibit the corrosion of aluminium and reduce evolution of hydrogen gas in aqueous solution of alkaline media ¹⁰. Schiff bases are good corrosion inhibitors ¹¹-¹². Mannich bases are also investigated as good corrosion inhibitor ¹³-¹⁵. All the above components are good corrosion inhibitors but these are costly, toxic, pollutant and harmful so we need eco-friendly inhibitors.

The naturally occurring plant products are eco-friendly, compatible, nonpolluting, less toxic, easily available, biodegradable and economic to be used as corrosion inhibitor. A number of natural products extracted from plants are also found effective corrosion inhibitor like: Argemone mexicana ¹⁶, Withania somnifera ¹⁷, Holly Basil ¹⁸-¹⁹, Ocimum sanctum ²⁰ etc.

Euphorbia caducifolia is a Euphorbiaceae species native to Thar Desert of India, where latex of E. caducifolia (ECL) is used by the local inhabitants for treatment of bleeding wound, cutaneous eruption and other skin diseases ²¹. Isolated fraction of E. caducifolia (IFEC) and latex of E. caducifolia (ECL) were tested against S. aureus, M. luteus, B. subtilis, E. coli, S. typhi, A. niger and C. albicans ²². Flower extract of Euphorbia caducifolia ²³ is found effective corrosion inhibitor for iron in different acidic media like sulphuric acid, nitric acid and hydrochloric acid. Leaf, stem and flower extract of Euphorbia caducifolia ²⁴ are also effective corrosion inhibitor for aluminium in HCL. In the proposed investigation...
Euphorbia caducifolia extract will be used as corrosion inhibitor in nitric acid on aluminium.

Plant Description

Euphorbia caducifolia is native to Thar desert of India and located on rocky terrain, hills. It is also called “Thor” and “Danda-thor”.

Extract of euphorbia caducifolia is widely used in medicines. It is used for treatment of bleeding wound, cutaneous eruption, urinary problems, kidney stones, rheumatic pain, jaundice, diabetes, stomach pain, hernia etc.

It contains caudicifolin (8,14-epoxy-17-hydroxy-11,13(15)-abietadien-15,12-olide) norcycloartane type triterpene, cyclocaducinol, triterpenes euphol, tirucallol and cycloartenol.

Experimental

Square specimen of aluminium of dimension 2.5x2.5 cm² containing a small hole of about 2mm diameter near the upper edge were used for studying of corrosion. Different solutions of HNO₃ were prepared using double distilled water.

Each specimen was suspended by a V shaped glass hook made of fine capillary tube and immersed in the beaker containing 100 ml of uninhibited and different concentration of inhibited test solutions. After the sufficient exposure, the specimen were taken out, washed thoroughly with running water and then dried with hot air dryer and then the final weight of each specimen was taken.

The percentage inhibition efficiency was calculated as

$$\eta \% = \frac{\Delta W_u - \Delta W_i}{\Delta W_i} \times 100$$

and surface coverage ($\theta$) was calculated as

$$\theta = \frac{\Delta W_u}{\Delta W_i}$$

Where $\Delta W_u$ is weight loss of metal in acid solution in the absence of inhibitor and $\Delta W_i$ is weight loss of metal in acid solution in the presence of known amount of inhibition.

The Corrosion rate (CR) in mm/yr can be obtained by following equation

$$R_{corr.} = \frac{\Delta W \times 87.6}{D \times A \times T}$$

Where $\Delta W$ = weight loss in milligrams, $D$ = metal density in g/cm³, $A$ = area of sample in cm², $T$ = time of exposure of the metal sample in hours.

Inhibition efficiency was also determined by thermometric method. In this method a specimen was immersed in a reaction chamber containing 100ml of solution at an initial temperature of 25°C. Temperature change were measured using a thermometer. Initially temperature increased slowly, then rapidly and attain a maximum value before falling. The maximum temperature was recorded.

Percentage inhibition efficiency were calculated as

$$\eta \% = \frac{RN_f - RN_i}{RN_f} \times 100$$

Where $RN_f$ and $RN_i$ are the reaction number in the absence and presence of inhibitor respectively and reaction number is defined as

$$RN = \frac{T_m - T_i}{t}$$

Where $T_m$ and $T_i$ are maximum and initial temperature and t is the time (in minutes) required to reach the maximum temperature.

Result and Discussion

Weight loss, percentage inhibition efficiency, surface coverage and corrosion rate in 1N, 1.5N, 2N and 2.5N HNO₃ solution with different concentration of leaf, stem and flower extract inhibitor are given in table1 and table 2.
### Table 1. Weight loss data ($\Delta W$) and percentage inhibition efficiency (%) for aluminium in 1N and 1.5N HNO$_3$ with inhibitor of leaf, stem and flower extract.

<table>
<thead>
<tr>
<th>Conc. Of inhibitor (%)</th>
<th>$\Delta W$ (g)</th>
<th>I.E. ($\eta$%)</th>
<th>Surface Coverage (θ)</th>
<th>Corrosion Rate</th>
<th>Log (0/1-θ)</th>
<th>Conc. Of inhibitor (%)</th>
<th>$\Delta W$ (g)</th>
<th>I.E. ($\eta$%)</th>
<th>Surface Coverage (θ)</th>
<th>Corrosion Rate</th>
<th>Log (0/1-θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leaf</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Leaf</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uninhibited</td>
<td>0.5216</td>
<td>0.00361</td>
<td>0.76052</td>
<td>0.2</td>
<td>0.0959</td>
<td>0.8131</td>
<td>0.00076</td>
<td>0.63853</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.0771</td>
<td>85.21</td>
<td>0.8521</td>
<td>0.00053</td>
<td>0.81191</td>
<td>0.8392</td>
<td>0.00066</td>
<td>0.71758</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.0696</td>
<td>86.64</td>
<td>0.8664</td>
<td>0.00048</td>
<td>0.81991</td>
<td>0.8634</td>
<td>0.00056</td>
<td>0.80076</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.0526</td>
<td>89.91</td>
<td>0.8991</td>
<td>0.00036</td>
<td>0.94991</td>
<td>0.8975</td>
<td>0.00042</td>
<td>0.94231</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>0.0408</td>
<td>92.17</td>
<td>0.9217</td>
<td>0.00028</td>
<td>1.07082</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stem</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Stem</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.0855</td>
<td>83.61</td>
<td>0.8361</td>
<td>0.00059</td>
<td>0.70768</td>
<td>0.2</td>
<td>0.1017</td>
<td>80.17</td>
<td>0.8017</td>
<td>0.00081</td>
<td>0.60669</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0784</td>
<td>84.96</td>
<td>0.8496</td>
<td>0.00054</td>
<td>0.75196</td>
<td>0.4</td>
<td>0.0925</td>
<td>81.97</td>
<td>0.8197</td>
<td>0.00074</td>
<td>0.65766</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0659</td>
<td>87.35</td>
<td>0.8735</td>
<td>0.00045</td>
<td>0.83917</td>
<td>0.6</td>
<td>0.0801</td>
<td>84.38</td>
<td>0.8438</td>
<td>0.00064</td>
<td>0.73255</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0494</td>
<td>90.53</td>
<td>0.9053</td>
<td>0.00034</td>
<td>0.98044</td>
<td>0.8</td>
<td>0.0632</td>
<td>87.68</td>
<td>0.8768</td>
<td>0.00050</td>
<td>0.85229</td>
</tr>
<tr>
<td><strong>Flower</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Flower</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1026</td>
<td>80.32</td>
<td>0.8032</td>
<td>0.00071</td>
<td>0.61080</td>
<td>0.2</td>
<td>0.1149</td>
<td>77.61</td>
<td>0.7761</td>
<td>0.00092</td>
<td>0.53986</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0930</td>
<td>82.16</td>
<td>0.8216</td>
<td>0.00064</td>
<td>0.66326</td>
<td>0.4</td>
<td>0.1064</td>
<td>79.26</td>
<td>0.7926</td>
<td>0.00085</td>
<td>0.58224</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0722</td>
<td>86.15</td>
<td>0.8615</td>
<td>0.00050</td>
<td>0.79380</td>
<td>0.6</td>
<td>0.0955</td>
<td>81.39</td>
<td>0.8139</td>
<td>0.00076</td>
<td>0.64082</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0524</td>
<td>89.94</td>
<td>0.8994</td>
<td>0.00033</td>
<td>0.95135</td>
<td>0.8</td>
<td>0.0748</td>
<td>85.42</td>
<td>0.8542</td>
<td>0.00059</td>
<td>0.76780</td>
</tr>
</tbody>
</table>

**Fig. 1.** Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 1N HNO$_3$.

**Fig. 2.** Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 1.5N HNO$_3$.
Table 2. Weight loss data ($\Delta W$) and percentage inhibition efficiency (%) for aluminium in 2N and 2.5N HNO$_3$ with inhibitor of leaf, stem and flower extract

<table>
<thead>
<tr>
<th>Temperature : 25±0.1°C</th>
<th>Area of Specimen : 13 cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N HNO$_3$ (264 hours)</td>
<td>2.5N HNO$_3$ (216 hours)</td>
</tr>
<tr>
<td>Conc. of inhibitor (%)</td>
<td>$\Delta W$ (g)</td>
</tr>
<tr>
<td>Leaf</td>
<td>Uninhibited</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1277</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1154</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1026</td>
</tr>
<tr>
<td>0.8</td>
<td>0.0891</td>
</tr>
<tr>
<td>Stem</td>
<td>Uninhibited</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1328</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1191</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1050</td>
</tr>
<tr>
<td>Flower</td>
<td>Uninhibited</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1430</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1290</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1177</td>
</tr>
</tbody>
</table>

Fig 3. Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 2N HNO$_3$.

Fig 4. Variation of inhibition efficiency with concentration of leaf, stem and flower extract for aluminium in 2.5N HNO$_3$. 

Table 3. Reaction number (RN) and inhibition efficiency (%) for aluminium in 2N, 3N and 4N HNO₃ with inhibitor of leaf, stem and flower extract.

<table>
<thead>
<tr>
<th>Conc.</th>
<th>2N HNO₃</th>
<th>3N HNO₃</th>
<th>4N HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RN</td>
<td>I.E. (%)</td>
<td>RN</td>
</tr>
<tr>
<td>Leaf</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uninhibited</td>
<td>0.3654</td>
<td>0.6456</td>
<td>0.9412</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1702</td>
<td>53.42</td>
<td>0.3297</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1638</td>
<td>55.16</td>
<td>0.3128</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1485</td>
<td>59.34</td>
<td>0.2959</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1370</td>
<td>62.51</td>
<td>0.2663</td>
</tr>
<tr>
<td>Stem</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1820</td>
<td>50.18</td>
<td>0.3555</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1731</td>
<td>52.63</td>
<td>0.3432</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1597</td>
<td>56.29</td>
<td>0.3252</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1481</td>
<td>59.46</td>
<td>0.2976</td>
</tr>
<tr>
<td>Flower</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1965</td>
<td>46.21</td>
<td>0.3733</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1803</td>
<td>50.64</td>
<td>0.3532</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1720</td>
<td>52.92</td>
<td>0.3380</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1617</td>
<td>55.75</td>
<td>0.3147</td>
</tr>
</tbody>
</table>

Fig 5. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 2N HNO₃.

Fig 6. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 3N HNO₃.

Fig 7. Variation of reaction number with concentration of leaf, stem and flower extract for aluminium in 4N HNO₃.
It can be seen from tables that inhibition efficiency of inhibitor increases with increasing concentration of inhibitor. The Maximum inhibition efficiency 92.17% was obtained in 1N HNO₃ at an inhibitor concentration of 0.8% for flower extract. Maximum inhibition efficiency for stem extract was found 90.53% in 1N HNO₃ with 0.8% corrosion inhibitor whereas maximum Inhibition efficiency for flower extract in 1N HNO₃ was obtained 89.94% with 0.8% corrosion inhibitor. The result shows that leaf extract have higher inhibition efficiency in HNO₃ than stem and flower.

The variation of percentage inhibition efficiency with inhibitor concentration is depicted graphically in fig-1, 2, 3 and 4 in 1N, 1.5N, 2N and 2.5N acid strength respectively for leaf, stem and flower extract. It indicates that the inhibition efficiency increases with increasing inhibitor concentration.

From table 1 and table 2 it is clear that the surface coverage increase with increasing concentration of inhibitor and corrosion rate decrease with increasing concentration of inhibitor.

Inhibition efficiencies were also determined by using thermometric method. Thermometric experiments were carried out at higher concentrations of acid i.e. 2N, 3N and 4N because no appreciable changes of temperature were observed at lower concentrations of acid. Results summarized in table 3 show a good agreement with the results obtained by weight loss method. The variation of reaction number (RN) with inhibitor concentration is depicted graphically in fig. 5, 6 and 7 for HNO₃. The maximum inhibition efficiency was obtained with the highest concentration of leaf extract inhibitor at lowest concentration of acid. Inhibition efficiency increases with increasing concentration of inhibitor and decreases with increasing concentration of acid. Both methods (weight loss as well as thermometric) show same trends in corrosion efficiency and results are in good agreement with each others.

Conclusion
A study of extract of euphorbia caducifolia has shown that to be better corrosion inhibitor for aluminium in HNO₃. Weight loss and thermometric methods were shown that inhibition efficiency of plant extract increases with increasing inhibitor concentration over the range 0.2% to 0.8% and it decreases with decreasing concentration of acid. The maximum inhibition efficiency was found up to 92.17% for aluminium in 1N HNO₃ at a concentration of 0.8% for leaf extract whereas it was 90.53% for stem extract and 89.94% for flower extract with same concentration i.e. 0.8%. Thus, it was concluded that leaf extract is a better corrosion inhibitor in HNO₃ than stem and flower extract.

Acknowledgement
One of the authors (Reena Sharma) is grateful to Department of Chemistry, S. P. C. Govt. College, Ajmer for laboratory assistance.

Bibliography