Corrosion Control by water-soluble extracts from leaves of economic plants

H. H. Rehan*

Water extracts from leaves of date palm, phoenix dactylifera, henna, Lawsonia inermis, and corn, Zea mays, were tested as corrosion inhibitors for steel, aluminum, copper and brass in acid chloride and sodium hydroxide solutions using weight loss, solution analysis and potential measurements. The inhibition action was found to critically depend on metal type and solution composition. Only, date palm and henna extracts were found highly effective in reducing corrosion rate of steel in acid chloride solutions and aluminum in sodium hydroxide solutions. The inhibition efficiency increased with increasing the concentration of the extract. The inhibition was interpreted in terms of chemisorption of some active ingredients in the leaves according to Temkin isotherm.

Key words: corrosion, inhibition, steel, aluminium, chemisorption

Introduction

Corrosion of metals is considered a serious problem in industry, constructions and civil services, such as electricity, water and sewage supplies [1]. To prevent or minimize corrosion, inhibitors sometimes are used, especially in flow and closed systems, such as heat exchangers and cooling towers. Corrosion inhibitors may be organic, inorganic or a mixture of both, and work in one or more of the following ways; chemisorption on the corroding metal, reacting with the metal ions and forming a barrier-type precipitate on the surface or promoting passivity [2–8]. Being safe to man and friend to environment is a vital criterion for an inhibitor to be used on large scale. Stimulated by the public criticism of synthesized chemicals, the search for inhibitors derived from natural products seems to be interesting.

In the present study, water-extracts from the dry leaves of some economic plants are introduced as safe and cheap corrosion inhibitors for commercial grade metals; steel, aluminum, copper and brass. The plants are date palm, (phoenix dactyligera), henna (Lawsonia inermis) and corn (Zea mays). Leaves of date palm and corn are considered by-products and used chiefly in Basketry and animal feeding, respectively. Henna leaves are used in west Asia and Africa [9, 10] as a hair dyestuff (orange red due to the coloring material in henna leaves, 2-hydroxy-1,4-naphthoquinone) and used in shampoo industry, due to the pleasant dermatological effect [11, 14].

Experimental

Specifications of the metals used in the study are given in Table 1. Sheets with a thickness of 0.5–1.5 mm and a typical surface area of ca. 2 × 5.0 × 2.0 cm² were used for testing the corrosion inhibition efficiency of the extracts. The metal specimens were mechanically polished with successively finer grades of emery papers until scratches-free surfaces were obtained. The specimens were then degreased with acetone, washed thoroughly with distilled water, dried with a jet of hot air, weighed and introduced into the corrosive solution. The corrosive solutions were prepared from analytical grade HCl, KOH and NaCl and distilled water. Water-extracts of the following three economic plants were used; date palm (phoenix dactyligera, tree of the palm family Areaceae), henna (Lawsonia inermis, family Lythraceae) and corn (also called Maize, Zea mays, cereal plant, tribe Maydeae, grass family Gramineae, Poaceae). Green leaves from several local brands of date palms, corn plants and Henna trees were collected, washed, dried and powdered. The powders were sieved using sieves (500 μm = 32 mesh) and dried to constant weight at

<table>
<thead>
<tr>
<th>Table 1. Specification of the metals used in the study</th>
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<tbody>
<tr>
<td>Metal</td>
</tr>
<tr>
<td>Aluminum</td>
</tr>
<tr>
<td>Steel</td>
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<tr>
<td>Copper</td>
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<tr>
<td>Brass</td>
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102 °C. Each of the studied economic plants have many commercial hybrids (brands or sub-species) which may differ from a place to another in size, shape and products and a rigorous standardization of the leaves collected was difficult. For simplicity, several leaves samples from different brands of each plant (widely available in Arab peninsula and Middle East) were collected just before flowering (date palm: 5 samples, henna: 4 samples and corn: 3 samples). Preliminary investigations showed no significant effect of the brand type on the inhibition percent (maximum difference was 3%). Thus, one brand of each plant was used in the rest of the study. The extracts were prepared by occasional shaking of 5.0 g of the leaves’ powder in 1.0 litre of the corrosive solution for a day before filtration. Extracts with different concentrations (100%, 75%, 50%, 25%, 10%, 5%, 2.5%, 1%, 0.5% and 0.1%) were prepared from the 100% extract with the appropriate dilution with the corresponding corrosive solution.

In a typical experiment, the specimen was immersed in bakets containing 90 ml portions of the corrosive solution, without or with the inhibitor, covered with glass lids and left at the room temperature for the pre-defined time period. Thereafter, the specimens were cleaned with a tooth brush under running water, dried and weighed. Sometimes, portions of the corrosive solution were taken for metal ion analysis with atomic absorption. The reported weight loss was the average of three trails, with a tolerable difference ≤ 5%. The inhibition percent, 1%, was evaluated from the relation:

$$1\% = \left(\frac{R^* - R_{\text{extract}}}{R^*}\right) \times 1000 \quad (1)$$

Where $R^*$ and $R_{\text{extract}}$ are the corrosion rates in the absence and presence of the extract, respectively. In some cases, the corrosion potential, $E_{\text{corr}}$, of the metal specimen was recorded versus a saturated calomel electrode (SCE) after one and 24 hours. Unless otherwise stated, all tests were conducted at 25 ± 0.2 °C.

Results and Discussion
Effect of extract type

Weight losses determined by balance and solution analysis after a day of corrosion in the absence and presence of the extracts and the inhibition percents are given in Table 2. Balance and solution analysis (given between Parentheses) results were comparable, indicating that most of the corrosion products went into solution. However, solution analysis results were slightly higher than those determined by balance, due to the precipitation of some corrosion products on the corroding metals. In 0.2 M HCl, extracts from leaves of date palm

<table>
<thead>
<tr>
<th>Metal</th>
<th>ΔW (+)</th>
<th>Henna</th>
<th>Date Palm</th>
<th>Corn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔW</td>
<td>I%</td>
<td>ΔW</td>
<td>I%</td>
</tr>
<tr>
<td>Steel</td>
<td>5.40</td>
<td>0.75</td>
<td>86.1</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>(5.51)</td>
<td>(0.81)</td>
<td>(85.3)</td>
<td>(1.21)</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.32</td>
<td>1.14</td>
<td>*</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>(1.14)</td>
<td>(1.22)</td>
<td>(*)</td>
<td>(0.75)</td>
</tr>
<tr>
<td>Copper</td>
<td>1.29</td>
<td>0.88</td>
<td>31.8</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>(1.31)</td>
<td>(0.92)</td>
<td>(29.8)</td>
<td>(1.07)</td>
</tr>
<tr>
<td>Brass</td>
<td>0.89</td>
<td>0.71</td>
<td>19.1</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>(1.03)</td>
<td>(0.85)</td>
<td>(17.5)</td>
<td>(0.83)</td>
</tr>
</tbody>
</table>

0.2 M KOH

<table>
<thead>
<tr>
<th>Metal</th>
<th>ΔW (+)</th>
<th>Henna</th>
<th>Date Palm</th>
<th>Corn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔW</td>
<td>I%</td>
<td>ΔW</td>
<td>I%</td>
</tr>
<tr>
<td>Aluminum</td>
<td>31.70</td>
<td>1.27</td>
<td>96.0</td>
<td>9.32</td>
</tr>
<tr>
<td></td>
<td>(32.30)</td>
<td>(1.31)</td>
<td>(95.9)</td>
<td>(10.1)</td>
</tr>
</tbody>
</table>

*) No inhibition

Table 2. Weight loss, ΔW, for different metals in the absence and presence of extracts from leaves of three economic plants at 25 °C

and henna were effective inhibitors for steel and much less effective or not inhibitor at all for the other metals. The corn and henna extracts could not inhibit the corrosion of aluminum. The corn extract is the least effective inhibitor for all metals studied. In 0.2 M KOH, the corrosion of aluminum (the only studied metal in this solution) was pronouncedly suppressed with the henna extract and decreased to a lesser extent with the date palm extract. Again, the corn extract was practically inefficient inhibitor for corrosion of aluminum in 0.2 M KOH solutions. The results in Table 2 suggest that only henna and date palm extracts could be practical and efficient inhibitors in two cases; steel in acid solutions and aluminum in alkaline solutions. These two cases will be discussed further in the next sections.

Effect of time

Figs. 1 and 2 show the variation of weight loss, $\Delta W$, and the inhibition percent, 1%, for steel in 0.2 HCl and aluminum in 0.2 M KOH. The corrosion rate decreased with time in the absence and presence of the extracts, probably due to the partial blocking of the corroding surface by some precipitation of the corrosion products (mainly oxides). The maximum 1% was reached after a day and became practically constant with the seven days of study.

Effect of pH

The inhibition efficiency of the extracts from henna and date palm leaves for steel in HCl-NaCl solutions of different pH and a total chloride concentration of 1 mol/liter was studied. Fig. 3 shows the variation of $\Delta W$ and 1% with pH. The corrosion rate decreased with increasing pH as expected for a metal the corrosion of which is controlled by the cathodic processes of hydrogen evolution and O$_2$ reduction [15]. 1% showed a slight increase with pH. Previous studies on organic inhibitors showed a similar effect and the increase in 1% with pH was attributed to the partial deactivation of inhibitor species via protonation of some electron donating centers, such as nitrogen in amino-compounds and sulfur in thioc-compounds [7, 8, 16]. It is assumed that decrease in 1% of the extracts with increasing acidity (pH decrease) is due to protonation of some of the active sites in the ingredients involved in inhibition. Corrosion of aluminum in 0.5 M KOH in the absence and presence of the extracts revealed nearly the same inhibition percent recorded when 0.2 M KOH was used. Thus, one concludes that the inhibition action of the extracts is not due to alternation of the medium aggressiveness, i.e. suppression of acidity (or alkalinity) level via neutralization of some basic (or acidic) ingredients in the leaves with the acid (or alkali) used as corrosive medium.

Effect of extract concentration

The effect of concentration of the extracts of henna and date palm leaves on the inhibition efficiency was studied over two orders of magnitudes for steel in 0.2 M HCl and aluminum in 0.2 M KOH. As can be seen in Figs. 4 and 5, 1% increases linearly with increasing the extract concentration percent over the entire concentration range in all cases, except for the case of the extract of date palm with aluminum. In all cases, no leveling off (saturation) was observed, i.e. the maximum 1% of the extracts was not reached with the 100% extract and higher 1% may be expected if more active ingredients could be extracted from the leaves. The results seem to be consistent more or less with an inhibition mechanism involving chemisorption of some ingredients in the leaves of henna and date palm. This is because 1% increased with increasing the concentration of the extract concentration as usually observed.
in adsorption processes. It is customary in studies on adsorption inhibitors to consider a direct proportionation between I% and the surface coverage, $\theta$, with a monolayer of the adsorbed inhibiting species [8, 17, 18] and most chemisorption isotherms take the following form:

$$K_C = f(\theta)$$

(2)

where $K$ and $C$ are the equilibrium constant and concentration, respectively. The simplest adsorption isotherm is the Langmuir isotherm:

$$K_C = \frac{\theta}{(1 - \theta)}$$

(3)

Over a wide range of inhibitor concentration, Temkin isotherm, which takes the effect of $\theta$ on the heat of adsorption, $\Delta H_{ads}^{\circ}$, into consideration, found many applications [17, 19, 20]:

$$\theta = \frac{1}{\beta} \ln (K_C)$$

(4)

where $\beta$ is constant given in the assumption:

$$\Delta H_{ads}^{\circ} = \Delta H_{ads}^{\circ} (1 - \beta \theta)$$

(5)

where $\Delta H_{ads}^{\circ}$ is the heat of adsorption at $\theta = 1$. The results of steel seem to be more straightforward with the assumption of chemisorption mechanism rather than aluminum results. For

Fig. 4. Dependence of the inhibition percent, I%, on logarithm of the extract concentration percent for steel in 0.2 M HCl. Corrosion time was 24 hours.

Fig. 5. Dependence of the inhibition percent, I%, on logarithm of the extract concentration percent for aluminum in 0.2 M KOH. Corrosion time was 24 hours.

Fig. 6. Dependence of the corrosion potential, $E_{corr}$, on logarithm of the extract concentration percent. Upper) Aluminum in 0.2 M KOH and Lower) Steel in 0.2 M HCl. ◯, ● Henna and ▲, △ Dates palm. Closed symbols) one hour and Open symbols) 24 hours.
Effect of temperature

The effect of temperature (25–45 °C) on the corrosion rate of steel in 0.2 M HCl in the absence and presence of the extracts of henna and date palm (50%, 10% and 1%) was studied. The corresponding Arrhenius plots shown in Fig. 7 were used to calculate the activation energy of corrosion, $E_a$. $E_a$ values in the presence of the extracts were higher than in their absence and increased with increasing the extract concentration (Table 3). The $E_a$ values indicate that the corrosion of steel in 0.2 M HCl is controlled by diffusion processes, most probably, of the depolarizer species (H$^+$ ions and O$_2$). Partial blocking of the cathodic sites on the corroding surface by the adsorbed species from the extracts, in an amount which was proportional to concentration of the extract, lead to the increase in $E_a$. The variation of $\theta$ (equivalent to 1%) with the extract concentration at different temperatures (Fig. 8) yielded straight lines according to equation (4), from which apparent K values were determined. Although the true K value could not be determined in this study, since a relative concentration term was used, the heat of adsorption, $\Delta H_{ads}$, however, could be determined from the thermodynamic relation:

$$\ln K = -\frac{\Delta H_{ads}}{RT} + \text{constant}$$

(6)

The $\Delta H_{ads}$ values given in Table 3 are higher than 20 kcal mol$^{-1}$ and support the assumption of chemisorption process as the cause of inhibition of steel in acid solutions.

Conclusion

Water extracts from leaves of henna and date palm were found effective in suppression of corrosion of steel in acid chloride solutions and aluminum in potassium hydroxide solutions. It is assumed that the inhibition occurred mainly via chemisorption of some active ingredients in the leaves.
Table 3. Activation energy, $E_a$, of corrosion of steel in 0.2 M HCl and heat of adsorption, $\Delta H_{ad}$, of surface active substances in extracts of henna and date palm leaves

<table>
<thead>
<tr>
<th>Corrosive solution</th>
<th>$E_a$ / kcal mol$^{-1}$</th>
<th>$\Delta H_{ad}$ / kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without extract</td>
<td>4.983</td>
<td>26.521</td>
</tr>
<tr>
<td>With Henna extract</td>
<td></td>
<td>26.521</td>
</tr>
<tr>
<td>50%</td>
<td>11.756</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>10.350</td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>9.328</td>
<td></td>
</tr>
<tr>
<td>With Date Palm extract</td>
<td></td>
<td>21.645</td>
</tr>
<tr>
<td>50%</td>
<td>13.544</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>11.737</td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>9.839</td>
<td></td>
</tr>
</tbody>
</table>

References


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[T 537]

Neues aus der Galvanik: Effektiver Schutz gegen Korrosion!

Alternative zum Brünen und Phosphatieren

OFFTECH kombiniert eine neuartige Dünnverzinkung (unter 5 μm) mit anschließender Schwachzromatierung

Die Vorteile:
- Erhöhter Korrosionsschutz durch Kombination der Verfahren
- Passgenauigkeit der Teile dank dünner Zinkschicht unter 5 μm
- Salzsprühnebeltest: Schwachzromatierte Gestellware bis zu 48 Std. ohne Zinkkorrosion (Weiβrost)
- Produktionsfenster für Gestellware: 3000 × 1250 × 450 mm, Stückgewicht bis 400 Kg
- Besondere Wirtschaftlichkeit

Allein in Deutschland entstehen jährlich Verluste in Milliardenhöhe durch Korrosion (Rost) an Stahlteilen. Umso brenzlicher ist die Situation, wenn es sich um tragende oder systemkritische Bauteile handelt. Aus wirtschaftlichen und sicherheitstechnischen Gründen steigen die Anforderungen an effektive Korrosionsschutz-Systeme stetig an.

Der Oberflächenexperte OFFTECH aus Troisdorf bei Köln hat reagiert und schafft Abhilfe: In einem neuartigen Verfahren kombiniert er eine Dünnverzinkung mit einer anschließenden Schwachzromatierung. Der Clou: Die Zinkschicht ist dünner als 5 μm, so dass auf jeden Fall die Passgenauigkeit der Teile erhalten bleibt. Damit entfällt das sonst übliche Abdecken der Passflächen vor dem Verzinken.

Die anschließende Schwachzromatierung sorgt für ein dunkles Aussehen und erfüllt die gewünschte optische Funktion. Schwachzromatierte Teile müssen nicht geölt werden oder zu brünierte Teile, die lediglich hauchdünn eingefärbt sind. Und im Salzsprühnebeltest bleibt schwachzromatierte Gestellware bis zu 48 Stunden ohne Zinkkorrosion (Weiβrost) – im Gegensatz zu phosphatierten Teilen, wo sich bereits nach 1,5 Stunden Rotrost einstellt.

Wer also auf der Suche nach einem effektiven und kostengünstigen Korrosionsschutz ist, hat mit der galvanischen Dünnverzinkung mit anschließender Schwachzromatierung eine echte Alternative an der Hand.

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