Water Hyacinth as Corrosion Inhibitor in 1M HCl for Mild Steel

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Abstract: The inhibition efficiency of aqueous extract solutions of water hyacinth was investigated by weight loss method at 37°C. The values of inhibition efficiency were found dependent on the concentration of inhibitor. A decrease in corrosion rate and increase in inhibition efficiency were observed with increase in concentration of the inhibitor. Inhibition efficiency increased regularly with increasing concentration until reached to maximum. The maximum inhibition was found 97.7% at about 7 percent concentration of inhibitor. The increased inhibition was explained on the basis of adsorption isotherms. The decreased corrosion rate and adsorption behavior have been explained by Langmuir, Temkin and Freundlich adsorption isotherm. The constituents responsible for inhibition which were adsorbed on the surface of the metal were identified by Phytochemical analysis and Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy.

Keywords: Water hyacinth, Jalkumbhi, corrosion inhibitor, mild steel, adsorption, weight loss, Langmuir, Temkin isotherm, FTIR.

Introduction

It is a natural process of metal to corrode when exposed to severe environment like acidic medium of low pH. A very important and crucial stage of finishing of metal surface is pickling and descaling in which metals are treated with acids. Since most of the metals undergo corrosion in acidic medium especially mild steel, so a certain level of protection is required. Mild steel is frequently used in machinery and other structural manufacturing units [1, 2]. A number of organic compounds, natural and synthetic, serve the purpose of protecting metal from corrosion [3-7]. Many organic compounds, both natural and synthetic; have ability to adsorb on the surface of metal forming a barrier to further corrosion due to presence of hetero atoms [8-20]. Such organic compounds are termed as corrosion inhibitors.

Water hyacinth grows in all types of freshwaters environments. Water hyacinth poses a variety of negative impacts once introduced into a freshwater environment. This aquatic species is a menace to aquatic bodies. It cannot be eradicated completely. Some studies on water hyacinth have been carried out for its corrosion inhibition activity. The results showed protective nature of this natural product against corrosion in various corrosive environments [21-23]. It is a mixed type inhibitor. The positive aspect is that the natural poly phenols present in extract of water hyacinth was found to have good corrosion inhibition ability in acidic medium.

The present work deals with the corrosion inhibition and adsorption behavior of constituents of Water Hyacinth extract as an eco-friendly inhibitor. The work was carried out in 1M HCl at 37°C. Rate of corrosion, and inhibition efficiency were calculated by weight loss method. FTIR spectroscopic studies were carried out to investigate the compound adsorbed on the surface of metal.

Experimental

Materials and Methods

Alloy Used
Commercially available mild steel (C 0.15% by weight) was used for all experiments. The mild steel sheet was mechanically press-cut into 2.5x2.5x0.1 cm coupons. The steel coupons pickled with 5% HCl to remove rust and sequentially polished using Silicon Carbide emery papers of grade 180, 220, 400, 600 and 1000, washed thoroughly with distilled water and degreased with carbon tetra chloride and acetone.

Chemicals Used
1M HCl solutions were prepared using analytical grade concentrated 37% HCl (Merck products) respectively and double distilled water.

Preparation of Plant Extract
Fresh leaves of Water Hyacinth were collected from Ramgarhtal lake of Gorakhpur city in U.P., India. The green leaves were air-dried and then kept in an oven maintained at 105°C for constant weight to remove the moisture content. Dried leaves were crushed and ground in an electric operated grinder to make fine powder. Extract was prepared in 1M HCl for investigation. 50 g of dried powder of leaves were digested in 1000 mL 1M HCl and kept overnight. After 48 hours of soaking, it was filtered and the filtrate volume was made up to 1000 mL using 1M HCl. The extract so prepared was taken as stock solutions from which 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 % test solutions were prepared.

Phytochemical Screening

Test for Tannin
1 g of powdered sample was boiled with 20 ml distilled water for five minutes in a water bath and is filtered while hot.
1 ml of filtrate was diluted to 5 ml with distilled water and a few drops of 10% ferric chloride are added and observed. A bluish-black or brownish-green precipitate indicated the presence of tannins [24].

**Test for flavonoids**

1 g of the powdered dried leaves of sample is boiled with 10 ml of distilled water for 5 minutes and filtered while hot. Few drops of 20% sodium hydroxide solution were added to 1 ml of the cooled filtrate. A change to yellow colour which on addition of acid changed to colourless solution indicates the presence of flavonoids and also confirmed by analyzing about 3 ml of dilute ammonia was added to 2 ml aqueous filtrate of plant extract. This was followed by addition of 1 ml concentrated sulphuric acid (H₂SO₄). Yellow coloration in extract showed the presence of flavonoids [25].

**Weight Loss Studies**

The weight loss studies were carried out at 37°C by immersing steel coupons of known weight and surface area in 100 ml each of blank 1M HCl and tests solutions containing various concentrations of extracts for 48 hours. The dissolution of iron takes place as follows with subsequent release of hydrogen gas.

\[
\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2 \uparrow
\]

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}
\]

After 48 hours of reaction in absence and presence of different concentrations of extracts, the specimens were taken out, washed with water, dried and weighed. Corrosion rates (in terms of g.cm⁻²h⁻¹) were calculated using following expression.

\[
\text{Corrosion rate (CR)} = \frac{\text{Wi} - \text{Wf}}{\text{Surface area (cm}^2\text{)} \times \text{Time (h)}}
\]

Where, \(W_i\) = initial weight of coupon, \(W_f\) = weight of coupons after treatment \(W_f - W_i\) = weight loss (g)

The surface coverage (θ) as a result of adsorption of inhibitor and inhibition efficiency (η %) were calculated from corrosion rates using the following expression:

\[
\theta = \frac{\text{CR (Blank)} - \text{CR (Inhibitor)}}{\text{CR (Blank)}}
\]

\[
\% \eta = \frac{\text{CR (Blank)} - \text{CR (Inhibitor)}}{\text{CR (Blank)}} \times 100
\]

Where, 
\(\text{CR}_{\text{blank}}\) = corrosion rate in absence of inhibitor
\(\text{CR}_{\text{blankinhib}}\) = corrosion rate in presence of the inhibitor

**Fourier Transform Infrared Spectroscopy (FTIR)**

The identification of the corrosion inhibitor components in the extract was carried out by FTIR spectroscopy. FTIR spectra were recorded for aqueous extract of the leaves of water hyacinth.

**Results and Discussion**

**Analysis in 1M HCl**

Table 1 shows the variation of corrosion rate, surface coverage (θ) and percent inhibition efficiency (η %) in 1M HCl at 37°C for 48 hours studies. The graphs were plotted for corrosion rate and percent inhibition efficiency.

Figure-1 indicated that the corrosion rates were significantly lowered down in presence of inhibitor. The corrosion rate decreased with increasing extract concentration. The maximum lowering in corrosion rate was calculated in presence of 7% leaf extract of water hyacinth. 7% of extract concentration was also evaluated as the optimum concentration as on increasing the extract concentration above this no significant change in corrosion rate lowering was observed. Figure-2 showed that In case of leaf extract of the inhibitor maximum inhibition efficiency (97.7%) was noticed and no considerable change in inhibition efficiency was observed after this.

It has also been observed that the rate of inhibition in initial concentration of inhibitor 0.1% to 1.0% is more pronounced as compared to higher concentration. The surface coverage data indicated that the extent of adsorption was rapid and more significant at initial stage of adsorption.

Table 2 and figure-3 show the stability of corrosion inhibition which was determined by monitoring the test sample by keeping in corrosive 1M HCl solution in presence of 7% aqueous extract of Water Hyacinth corrosion inhibitor at 37°C. A regular increase with very slight variation of inhibition efficiency revealed that the adsorption of inhibitor is quite stable. Since the adsorption is constantly increasing with very nominal amount with the duration of exposure, it indicates the adsorption is of chemisorption nature in which molecules are bonded and adhered well on the surface giving metal an excellent protection. The chemisorptions was also confirmed by obeying the Langmuir adsorption isotherm [26].

Adsorption is the well-known phenomenon in which certain molecules get attached to the surface of metal through coordinate bonding. The hetero atoms having lone pair of electrons play significant role in adsorption [27]. The decreasing corrosion rate and increasing inhibition efficiency was attributed to the fact that the adsorption of inhibitor on the metal surface. Adsorption of compounds present in water hyacinth extract depends on its chemical constituents present in the aqueous extract. The phytochemical analysis revealed that the presence of tannins and phenolic compounds might be the possible reason for inhibition. It was further
confirmed by FTIR spectroscopic studies. Polyphenolic naturally occurring compounds, which have oxygen atoms with lone pair of electrons for coordinate bonding on the surface of metal are responsible for corrosion inhibition.

Table-1: Corrosion rate, surface coverage and percent inhibition efficiency of aqueous extract of water hyacinth leaves in 1M HCl at 37°C for 48 hours studies.

<table>
<thead>
<tr>
<th>Extract conc. %</th>
<th>Corrosion Rate (g cm⁻²h⁻¹) 10⁻⁵</th>
<th>Surface Coverage (θ)</th>
<th>% Inhibition efficiency (η)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>96.3</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.1</td>
<td>59.5</td>
<td>0.382</td>
<td>38.2</td>
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<tr>
<td>0.2</td>
<td>48.2</td>
<td>0.499</td>
<td>49.9</td>
</tr>
<tr>
<td>0.3</td>
<td>33.2</td>
<td>0.655</td>
<td>65.5</td>
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<tr>
<td>0.4</td>
<td>29.1</td>
<td>0.698</td>
<td>69.8</td>
</tr>
<tr>
<td>0.5</td>
<td>20.4</td>
<td>0.788</td>
<td>78.8</td>
</tr>
<tr>
<td>1.0</td>
<td>16.7</td>
<td>0.826</td>
<td>82.6</td>
</tr>
<tr>
<td>2.0</td>
<td>11.5</td>
<td>0.880</td>
<td>88.0</td>
</tr>
<tr>
<td>3.0</td>
<td>8.8</td>
<td>0.909</td>
<td>90.9</td>
</tr>
<tr>
<td>4.0</td>
<td>5.2</td>
<td>0.946</td>
<td>94.6</td>
</tr>
<tr>
<td>5.0</td>
<td>3.5</td>
<td>0.963</td>
<td>96.3</td>
</tr>
<tr>
<td>6.0</td>
<td>2.7</td>
<td>0.972</td>
<td>97.2</td>
</tr>
<tr>
<td>7.0</td>
<td>2.2</td>
<td>0.977</td>
<td>97.7</td>
</tr>
<tr>
<td>8.0</td>
<td>2.3</td>
<td>0.976</td>
<td>97.6</td>
</tr>
<tr>
<td>9.0</td>
<td>2.2</td>
<td>0.977</td>
<td>97.7</td>
</tr>
<tr>
<td>10.0</td>
<td>2.3</td>
<td>0.976</td>
<td>97.6</td>
</tr>
</tbody>
</table>

Figure 1: Plot of Concentration versus Corrosion Rate in presence and absence of inhibitor
**Figure 2:** Plot of Concentration versus % Inhibition of Water Hyacinth Inhibitor

<table>
<thead>
<tr>
<th>Day</th>
<th>% Inhibition Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.48</td>
</tr>
<tr>
<td>2</td>
<td>99.52</td>
</tr>
<tr>
<td>3</td>
<td>99.58</td>
</tr>
<tr>
<td>4</td>
<td>99.59</td>
</tr>
<tr>
<td>5</td>
<td>99.60</td>
</tr>
<tr>
<td>6</td>
<td>99.62</td>
</tr>
<tr>
<td>7</td>
<td>99.64</td>
</tr>
</tbody>
</table>

Table-2: % Inhibition Efficiency observed for 7% concentration of aqueous extract of Water Hyacinth for consecutive 7 days of analysis.

**Figure 3:** Plot of % Inhibition Efficiency for 7 consecutive days at 7% concentration of inhibitor at 37°C.
FTIR Analysis of Leaf Extract

Figure 4 shows FTIR spectra. FTIR data for aqueous extract of leaves and prominent peaks are given as below. The data furnished relevant information that reflects the corrosion inhibition was due to adsorption of such groups present in the extract. The FTIR spectra confirmed the presence of phytochemicals containing functional groups, hydroxyl –OH at 3422.50 cm\(^{-1}\), carbonyl C=O stretching at 1661.56 cm\(^{-1}\), amine -C-N stretching at 1380.72 cm\(^{-1}\), and saccharide linkage O-C-O at 1077.25 cm\(^{-1}\). The FTIR spectra also included aromatic Ar-H stretching at 2925.26 cm\(^{-1}\), C-H stretching at 2857.04 and aromatic rings at 1598.60 cm\(^{-1}\).

**Flavanoids**

The phytochemical analysis showed the presence of Tannin and flavanoids. On the basis of FTIR spectra it has been inferred that certain polyphenols are present on the surface of metal that acted as a barrier and imposed inhibitory effect.

Flavanoids are the compounds with conjugated system; they have hetero atoms and carbonyl groups which are electron rich species which can readily get adsorbed on the surface of the metal to form a thin, stable and well adhered protective film.

Figure 5 - Langmuir Adsorption isotherm for Water Hyacinth
Adsorption Behavior

Langmuir Adsorption Isotherm
A plot of C/θ against Concentration C (Figure 5) showed a straight line indicating that adsorption follows the Langmuir adsorption isotherm. This trend of adsorption indicated the formation of a stable protective film of inhibitor on the surface of metal.

Freundlich Adsorption Isotherm
A plot between θ/1-θ & C showed a straight line indicating that the adsorption obeys a Freundlich adsorption isotherm (Figure 6).

Temkin Adsorption Isotherm
A plot between surface coverage θ and log C showed straight line indicating Temkin adsorption isotherm (Figure 7).

Conclusions
1. The aqueous extract of Water hyacinth (Jalkumbhi) has been found an excellent natural corrosion inhibitor for mild steel in 1 M HCl solution.
2. The corrosion rate significantly decreased and inhibition efficiency increased with increasing concentration of inhibitor.
3. The adsorption was of chemisorptions nature that provided a good protection.
4. He adsorbed molecules aware poly phenols which was identified by chemical analysis and FT-IR analysis.
5. The decreased corrosion rate was due to adsorption of plant extract which was discussed on the basis of Langmuir, Freundlich and Temkin adsorption isotherm.
References