ABSTRACT

The anticorrosion behavior of the aqueous extract of Fenugreek leaves has been investigated as mild steel corrosion inhibitor in Sulphuric acid medium. The weight loss method was performed for determination of corrosion rate at 298 K, 303 K, 308 K and 313 K temperatures. The results showed that increase of the inhibition efficiency with increasing the concentration of plant extract reaching 89.06% at 303 K in the presence of 4 g/L of extract and decreased with increasing the temperature. The surface analysis was performed by scanning electron microscope technique that confirmed the formation of a protective layer on the metal surface in the presence of the extract.

Keywords: Mild steel; Fenugreek leaves; Electrochemical attack; Weight loss method; Adsorption isotherm; SEM analysis

INTRODUCTION

Corrosion is the deterioration of metal by the chemical reaction when the metals come in contact with the atmosphere or moisture. Steel is used widely as a metal or alloy in various industrial applications and acid solutions are used in many industrial processes such as acid cleaning and acid descaling etc. Corrosion of steel in acidic medium is common phenomena. Generally the generation of metals is from ores or the compounds which occur naturally with very high energy or large amount of energy [1]. Corrosion inhibitors are the best option to protect metal by the electrochemical attack. To inhibit the corrosion various synthetic corrosion inhibitors came into existence but these are toxic and hazardous in nature [1,2]. The problem is widespread everywhere that these corrosion inhibitors are hazardous to environment as well as to human beings also. Plant extracts are used commonly now a day as corrosion inhibitor. Green corrosion inhibitors replace the organic and inorganic corrosion inhibitors [2-4]. These plant extracts are nontoxic in nature, easily available, cheap, and the most important thing is it is environment friendly. These plant extract contains organic ingredients or polar atoms like N, O, P and S [4]. A protective film is formed when these plant polar atoms works as a bridge between the plant extract and the metal surface [5]. These plant extract or green corrosion inhibitors contain many organic compounds and interact with the corroded metal by their electrons [6]. Due to which a protective film is formed and the corrosion is controlled. A great number of scientific studies have been dedicated to the corrosion of mild steel and the use of natural products as a corrosion inhibitors as Azadirachta indica [5], Sesamum indicum [6], Dodonaea viscosa (L.) [7], Justicia gendarussa [8], Wrightia tinctoria, Clerodendrum phlomidis, Ipomoea triloba [9], for mild steel in acidic media. The aim of this work was to investigate the inhibition effect of aqueous extract of fenugreek leaves as a corrosion inhibitor on the corrosion of mild steel in 1M H₂SO₄ solution at 298 K, 303 K, 308 K, and 313 K temperature by weight loss method.
MATERIALS AND METHODS

Preparation of Specimens
Mild steel specimens used in this experiment were cut from sheet with dimensions 5x2x0.1 cm. These coupons were polished with different grades emery papers after that washed with deionized water, degreased with acetone, dried and weighed before experiments.

Extract Preparation
Fresh Fenugreek leaves were used to make the aqueous extract. Fenugreek leaves purchased from local market, and dried in shades for 48 hours. The leaves powder weighed 50 g were thoroughly washed in distilled water and soaked in 500 ml. distilled water for 24 Hours then heated at 50-55°C and extract was filtered through Whatman No.1 filter paper. The extract of Fenugreek leaves obtained in this manner was used as an inhibitor. The extract were characterized by UV-Visible spectroscopy using a SHIMADZU UV-Visible 1800 spectrophotometer.

Solutions Preparation
The aggressive solutions were prepared from analytical grade reagents H₂SO₄ and de-ionized water. A stock solution was prepared using distilled water and 1 M H₂SO₄. The concentration range of Fenugreek leaves extract employed was varied from 1- 4 g/L.

Mass Loss Measurements
Weight loss method is mostly used for determination of corrosion rate. Mass loss experiments were performed at 298 K, 303 K, 308 K and 313 K with different concentrations of Fenugreek leaves extract for 6 hours immersion time. The Corrosion Rate (CR), Surface Coverage (θ) and Inhibition Efficiency (%IE) was calculated using the equation given below:

\[
\text{Corrosion Rate (mmpy)} = \frac{8.76 \times W}{DA \times T}
\]

Where, mmpy = millimeter per year, W = weight loss in milligrams, D = Density of steel (gm/cm³), A = Surface area of steel (cm²), T = Time of exposure in hours

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using equation (2) and equation (3), respectively.

\[
\% \text{IE} = \left( \frac{W_1 - W_2}{W_1} \right) \times 100
\]

\[
\theta = \left( \frac{W_1 - W_2}{W_1} \right)
\]

Where W₁ and W₂ are the corrosion rates in the absence and presence of the inhibitor respectively

RESULTS AND DISCUSSION

UV Analysis
The UV-VIS spectroscopy of the plant extract was studied at a wavelength range of 200 to 800 nm. One major band was recorded between 200-400 nm shows the presence of hetero atoms in extract (Figure 1).

Weight Loss Method
The Inhibition Efficiency (%IE) and corrosion rate in presence and absence in inhibitor at all temperatures are summarized in Tables 1-4 (Figures 2-8).

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mg/L)</th>
<th>Weight loss (W₁-W₂)</th>
<th>Corrosion Rate (mm/year)</th>
<th>Surface Coverage (θ)</th>
<th>Inhibition Efficiency (%IE)</th>
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<td>85.93</td>
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<tr>
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<td>70</td>
<td>13.01911</td>
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</table>
Figure 1: UV-Vis spectra of aqueous extract of fenugreek leaves

Table 2: Weight loss results of mild steel in 1 M H$_2$SO$_4$ in absence and presence of different concentrations of fenugreek leaves extract for 6 hours at 303 K

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mg/L)</th>
<th>Weight loss ($W_1$-$W_2$)</th>
<th>Corrosion Rate (mm/year)</th>
<th>Surface Coverage ($\theta$)</th>
<th>Inhibition Efficiency (%IE)</th>
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<td>29.75</td>
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<td>84.31</td>
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</table>

Table 3: Weight loss results of mild steel in 1 M H$_2$SO$_4$ in absence and presence of different concentrations of fenugreek leaves extract for 6 hours at 308 K

<table>
<thead>
<tr>
<th>Concentration of inhibitor (mg/L)</th>
<th>Weight loss ($W_1$-$W_2$)</th>
<th>Corrosion Rate (mm/year)</th>
<th>Surface Coverage ($\theta$)</th>
<th>Inhibition Efficiency (%IE)</th>
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</thead>
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<tr>
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Table 4: Weight loss results of mild steel in 1 M H$_2$SO$_4$ in absence and presence of different concentrations of fenugreek leaves extract for 6 hours at 313 K

<table>
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<tr>
<th>Concentration of inhibitor (mg/L)</th>
<th>Weight loss ($W_1$-$W_2$)</th>
<th>Corrosion Rate (mm/year)</th>
<th>Surface Coverage ($\theta$)</th>
<th>Inhibition Efficiency (%IE)</th>
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</table>
Figure 2: Concentration of inhibitor (g/L) and inhibition efficiency (%IE) of mild steel in various concentration of fenugreek leaves extract at 25°C (298 K) in 1 M H₂SO₄ solution

Figure 3: Concentration of inhibitor (g/L) and corrosion rate of mild steel in various concentration of fenugreek leaves extract at 25°C (298 K) in 1 M H₂SO₄ solution

Figure 4: Concentration of inhibitor (g/L) and inhibition efficiency (%IE) of mild steel in various concentration of fenugreek leaves extract at 30°C (303 K) in 1 M H₂SO₄ solution
Figure 5: Concentration of inhibitor (g/L) and corrosion rate of mild steel in various concentration of fenugreek leaves extract at 30°C (303 K) in 1 M H₂SO₄ solution

Figure 6: Concentration of inhibitor (g/L) and inhibition efficiency (%IE) of mild steel in various concentration of fenugreek leaves extract at 35°C (308 K) in 1 M H₂SO₄ solution

Figure 7: Concentration of inhibitor (g/L) and corrosion rate of mild steel in various concentration of fenugreek leaves extract at 35°C (308 K) in 1 M H₂SO₄ solution
The results are show that the CR is decreasing with increase in the concentration of inhibitor which indicates higher the adsorption of biomoleclues on metal surface. This means that corrosion rate decreases as we increase the concentration of inhibitor and reached a maximum value of 89.06% at a concentration of 4 g/L at 298 K. With the increase in the acid concentration the rate of corrosion increases which designates that the acid molecules are absorbed on the metal surface which impede the dissolution of latter by blocking its corrosion sites and hence decreasing the corrosion rate.

In order to study the effect of temperature on inhibition efficiency temperature investigation provides the information about the stability of the inhibitor film. The rate of corrosion at different temperatures is represented in Tables 1-4. Inspection of Figure 9 reveals that inhibition efficiency decreases with increase in temperature. In acidic medium, there is an evolution of H$_2$ gas, increase in temperature which accelerates the rate of corrosion reaction which results in dissolution of metal. The increase in corrosion rate on increasing temperature can be attributed due to etching, rupture and desorption of inhibitor molecules [9,10].

**Adsorption Isotherm**
The adsorption isotherm is very important for provide information about the interaction of bio molecules and surface of metal. It can be explained by using two type of interaction: physisorption and chemisorptions.
The Langmuir adsorption isotherm can be expressed by the Eq. 4 given below.

\[ \log \frac{C}{\theta} = \log C - \log K \]  

Where, inhibitor concentration is C, the fraction of the surface covered (\( \theta \)), adsorption coefficient \( K_{ads} \). The linear graph between \( \log C/\theta \) versus \( \log C \) were (Figure 10) indicating Langmuir adsorption.

The Langmuir isotherm showed a good linearity, this isotherm assumes that the metal surface contains a fixed number of adsorption sites and each site holds one adsorbate \([11,12]\). Since the linear regression coefficient/or correction factors \( (R^2) \) are unity (1) at 298 K and almost unity (0.996) at 303 K, (0.967) at 308 K and (0.943) at 313 K, the adsorption behavior is believed to have obeyed Langmuir adsorption isotherms.

**SEM Analysis**

SEM observations were performed to confirm the formation of a protective film of the Fenugreek leaves extract on the metal surface. The SEM images clearly shows in Figures 11a and 11b, the mild steel specimens exposed for 6 hours to 1 M H2SO4 solution in the presence and absence of 4 g/L of the leaves extract. After exposure to the corrosive acid media, the mild steel specimens exhibited a few cracks and irregularities on their surfaces, owing to acid corrosion. It is show that the corrosion reaction does not take place homogeneously over the surface of mild steel in acidic medium. However, the surface is remarkably protected by because of the formation of a protective layer of the adsorbed extract molecules on the specimen surface.
CONCLUSION

The tests performed in this study showed that the Fenugreek leaves extract acts as an efficient corrosion inhibitor for preventing corrosion of mild-steel in a 1M sulphuric acid. The increasing concentration of inhibitor reduces the corrosion of metal and attains a maximum 89.06%. The inhibitor adsorbed on metal surface and form a protective layer obeys Langmuir adsorption isotherm. SEM images also supported the formation of film on the metal surface.

REFERENCES