ABSTRACT

The inhibitive effect of *Musa acuminata* Red Dacca flower extract in 1N HCl / H$_2$SO$_4$ acid on mild steel was calculated using weight loss method and surface examination study by FTIR. The extract of the Red Dacca flower extract was subjected to preliminary phytochemical screening to identify the chemical constituents of the plant. The results revealed strong presence of tannins and steroids and moderate presence of, alkaloids, terpenoids, reducing sugar and coumarins. The corrosion inhibition efficiency studied showed that the inhibition efficiency increased with increase in the concentration of the extract. RD flower extract showed a maximum efficiency of 99.40% and 96.99% at 2.5 % v/v in 1N HCl and 1N H$_2$SO$_4$ respectively.

**Keywords:** *Musa acuminata* Red Dacca, flower extract, acid medium, mild steel, FTIR.

1. INTRODUCTION

Mild steel finds a wide range of applications in industries, because of its availability, low cost, ease of fabrication and high tensile strength. But mild steel has a high tendency to corrode easily (Vinod Kumar *et al.*, 2010). Use of inhibitors is one of the most practical methods for protection against corrosion. Present study deals with description of methods used in characterization of plant material and corrosion monitoring techniques. Corrosive inhibitive effect of flower extract of *Musa acuminata* Red Decca (Figure 1) in 1N HCl / H$_2$SO$_4$, on mild steel was carried out using conventional weight loss method and surface examination analysis (FTIR).

2. MATERIALS AND METHODS

2.1. Phytoanalysis

2.1.1. Collection of plant materials

Study was carried out on *Musa acuminata* Red Dacca flower extract, obtained from cultivated farm in Salem, Tamil Nadu, India. Dried sample was ground into powder (Figure 2) using an electronic blender, sieved and fine powder stored in air tight container.

2.1.2. Phytochemical screening

Extract of *Musa acuminata* Red Dacca flower extract was subjected to preliminary phytochemical screening to identify chemical constituents of plant, as described by various researchers Kotate (1999), Kotate 2010 and Harborne (1984, 1998).

2.2. Corrosion studies

2.2.1. Preparation of the Inhibitor

25 gm of dried powder of flower was boiled in 500ml of 1N HCl / H$_2$SO$_4$ acid with reflux condenser (Figure 3) for three hours and kept overnight to extract its phytounitents. Extract filtered and filtrate volume made up to 500ml using respective acids. Extract so prepared was taken as 5% stock solution and from this other concentrations were prepared.
Fig. 3. Photograph of Experimental Set up for Obtaining Plant Extract

2.2.2. Weight Loss Method

2.2.2.1. Preliminary treatment of mild steel

Rectangular mild steel coupons of size 5 × 1 × 0.2 cm (Figure 4) cut from a large sheet of mild steel, with a small hole of about 1.0mm diameter near the 1.5cm side end for suspending were polished using silicon carbide emery papers of grade 200, 400, 600, washed with distilled water, dried, degreased with acetone and dried and kept in desiccators to avoid adsorption of moisture.

Fig. 4. Photograph of Mild Steel Coupons

2.2.2.2. Immersion study

Weight loss studies were conducted at room temperature. Mild steel specimens were weighed accurately in electronic balance. After initial weighing, the specimens were fully immersed using glass hooks in beakers containing 100ml of 1N HCl/\(\text{H}_2\text{SO}_4\) without and with inhibitor of different concentrations (0.1, 0.5, 1.0, 1.5, 2.0, 2.5 % v/v) at various intervals of time (1, 3, 5, 7, 12 hours) (Figure 5). After the specified period of immersion, the specimens were removed, washed with distilled water, dried and reweighed.

2.3. Surface examination studies

Surface analysis studies FTIR of mild steel specimens were done in order to study changes that occur during corrosion of mild steel in presence and absence of inhibitor in acid media (Raja and Sethuraman, 2008, 2009).

Fig. 5. Photograph of specimens fully immersed in acid medium without and with inhibitor

2.3.1. Preparation of the specimen for surface analysis.

Mild steel specimens (5 ×1 × 0.2 cm) were abraded with emery paper of grade 400 and 600 to a mirror finish, washed with distilled water and then rinsed with acetone and dried by hot air drier (Hegazy et al., 2011).

2.3.2. Surface morphology studies by Fourier Transform Infrared spectroscopy

Mild steel specimens were immersed in 1N HCl / \(\text{H}_2\text{SO}_4\) solution in absence and presence of 2% v/v concentration of RD flower extracts for a period of three hours at room temperature, removed, washed carefully with distilled water without disturbing the surface and dried. FTIR spectra of the samples were taken at Bharathiar University, Coimbatore, India (Model : Shimadzu).

3. RESULTS AND DISCUSSION

3.1. Qualitative phytochemical analysis

Phytochemicals present in aqueous flower extract of Red Dacca are summarized in Table 1. Results indicated that reducing sugar, saponins, coumarins and steroids were moderately present in the RD (F) extract. RD (F) extract showed the active presence of alkaloids and terpenoid. Exceptional factor was tannin content seemed to be high in RDF extract of Red Dacca flower. It is evident from the tabulation that the other phytochemicals like carbohydrates, flavonoids, phlobotannins, cycloglycosides, total phenols, quinones and anthraquinones were absent in extract of Musa acuminate Red Dacca flower.

These results suggest the presence of primary bioactive metabolites of commercial importance which acts as the precursors for the synthesis of secondary metabolites. These in turn help in development of new bio products as corrosion inhibitor for future.
Table 1. Phytochemical constituents present in the extract of *Musa acuminata* Red Dacca flower

| Phytocompound       | RD (F) extract |
|---------------------|----------------|
| Carbohydrates       | +              |
| Reducing sugars     | ++             |
| Alkaloids           | +              |
| Saponins            | ++             |
| Tannins             | +++            |
| Flavonoids          | -              |
| Terpenoids          | +              |
| Phlobotannins       | -              |
| Coumarins           | ++             |
| Cycloglycosides     | -              |
| Total phenols       | -              |
| Quinones            | -              |
| Anthraquinones      | -              |
| Steroids            | ++             |

Key: ‘+++’ active compound copiously present, ‘++’ active compound moderately present, ‘+’ active compound present, ‘-’ active compound absent.

3.2. Weight loss studies

Mild steel was found to corrode in 1N HCl / H₂SO₄ acid solution. This was evidenced by the decrease in the original weight of the metal coupons. With addition of plant extract to the acids, it was found that weight loss decreases with increase in concentration from 0.1 to 2.5% v/v due to adsorption of plant nutrient and protects from dissolution of metal (Loto, 2011).

3.2.1. Effect of Concentration of RD flower Extract on Concentration Rate and Inhibition Efficiency

Variation of inhibition efficiency and corrosion rate with change in concentration of the inhibitor is presented in Table 2 and Table 3. It is obvious from the data that there was decrease in the corrosion rate with increase in the inhibitor concentration for all immersion periods. The decrease in corrosion rate and increase in inhibitor efficiency was usually attributed to the adsorption of flower extract constituents on the surface of mild steel which makes a barrier for mass and charge transfers and protects further attack by the acid (Saratha and Vasudha, 2009).

Table 2. CR of mild steel and IE of RD (F) extract in 1N HCl acid in various concentration and immersion period.

| Conc. of Extract (%) | 1h CR mm/y | 1h IE (%) | 3h CR mm/y | 3h IE (%) | 5h CR mm/y | 5h IE (%) | 7h CR mm/y | 7h IE (%) | 24h CR mm/y | 24h IE (%) |
|----------------------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|-------------|-----------|
| Blank                | 32.32      | -         | 35.66      | -         | 37.22      | -         | 44.73      | -         | 83.72       | -         |
| 0.1                  | 6.68       | 79.31     | 4.82       | 85.08     | 15.15      | 59.29     | 31.84      | 29.20     | 2.55        | 25.65     |
| 0.5                  | 5.57       | 84.56     | 2.22       | 93.13     | 4.68       | 87.42     | 3.82       | 91.37     | 2.46        | 28.27     |
| 1.0                  | 3.34       | 89.6      | 1.85       | 94.27     | 3.34       | 91.02     | 1.75       | 94.74     | 2.32        | 32.06     |
| 1.5                  | 3.34       | 90.62     | 1.48       | 95.40     | 2.00       | 94.62     | 1.91       | 95.72     | 2.04        | 40.52     |
| 2.0                  | 2.22       | 92.1      | 1.11       | 96.56     | 1.33       | 96.42     | 1.59       | 96.44     | 1.57        | 54.22     |
| 2.5                  | 1.20       | 93.1      | 0.74       | 97.70     | 0.22       | 99.40     | 1.11       | 97.51     | 1.48        | 56.85     |

Table 3. CR of mild steel and IE of RD (F) extract in 1N H₂SO₄ acid in various concentration and immersion period.

| Conc. of Extract (%) | 1h CR mm/y | 1h IE (%) | 3h CR mm/y | 3h IE (%) | 5h CR mm/y | 5h IE (%) | 7h CR mm/y | 7h IE (%) | 24h CR mm/y | 24h IE (%) |
|----------------------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|-------------|-----------|
| Blank                | 42.35      | -         | 75.22      | -         | 79.57      | -         | 79.28      | -         | 83.72       | -         |
| 0.1                  | 10.03      | 71.87     | 22.38      | 70.74     | 15.15      | 80.96     | 10.50      | 86.75     | 27.76       | 66.84     |
| 0.5                  | 7.80       | 78.12     | 9.93       | 88.03     | 10.47      | 86.84     | 7.80       | 90.16     | 23.77       | 71.60     |
| 1.0                  | 5.57       | 86.84     | 8.08       | 89.36     | 6.90       | 91.32     | 5.87       | 92.57     | 19.87       | 76.25     |
| 1.5                  | 4.45       | 89.49     | 7.05       | 90.64     | 5.34       | 93.28     | 3.98       | 94.97     | 16.85       | 79.87     |
| 2.0                  | 3.34       | 92.11     | 5.01       | 93.35     | 4.01       | 94.96     | 3.02       | 96.19     | 14.48       | 82.69     |
| 2.5                  | 2.22       | 94.22     | 4.17       | 94.68     | 3.78       | 95.24     | 2.38       | 96.99     | 13.83       | 83.47     |
3.2.2. Effect of Immersion Time on Corrosion Rate and Inhibition Efficiency

Variation of inhibitor efficiency with inhibitor concentration and immersion time is given in figure 6a and 6b. The inhibition efficiency increased with increase in concentration of the inhibitor from 0.1 to 2.5% at room temperature. The maximum inhibition efficiency was 99.40 % in case of RD (F) extract in 1N HCl for the immersion period of 5h and 96.99 % for RD (F) extract in 1N H$_2$SO$_4$ for the immersion period of 7h at a concentration of 2.5 %v/v. The decrease in inhibition efficiency thereafter with increasing time may be due to the shift in adsorption and desorption equilibrium which takes place simultaneously on prolonged exposure to the corrosive media (Putilova, 1960). These results suggest that the adsorption model arrangement and orientation of the constituents present in the Red Decca extract on the surface of mild steel may change with time (Rekha Nair, 2010). At low concentration, the aromatic rings of the phyto constituents may be oriented perpendicularly with respect to the metal surface. But at higher concentrations of inhibitor, the molecules may be reoriented to the parallel mode on the surface of mild steel. Therefore for higher concentration of inhibitor, more number of inhibitor molecules gets adsorbed on the surface of mild steel (Patel, 2009).

The adsorption of the phyto constituents on the metal surface makes a barrier for mass and charge transfers and thus protects the metal surface fraction occupied by the adsorbed molecules (Shymala and Arulanantham, 2009).

Table 4. FTIR peak values and possible functional group of adsorption layer formed on mild steel surface exposed to 1N HCl without and with RD (F) inhibitor.

| Mild Steel in 1N HCl Possible groups | Mild Steel in 1N HCl with RD(F) extract |
|--------------------------------------|----------------------------------------|
| Methylene CH asy/sym (S)              | 2850.27                                |
| Methoxy O-CH$_3$                      |                                        |
| Methyl ether C-H(S)                   | 2785.67                                |
| Methylamino                           |                                        |
| N-CH$_3$CH(S)                         |                                        |
| 2678.64                               | 2669.00                                |
| 2608.25                               |                                        |
| 2508.94                               |                                        |
| N-H ammonium ions                     | 2552.33                                |
| Multiple broad peaks                  | 2505.08                                |
| 2440.47                               | 2400.94                                |
| 2392.26                               | 2366.26                                |
| 2347.91                               |                                        |
| 2334.41                               |                                        |
Table 5. FTIR peak values and possible functional group of adsorption layer formed on mild steel surface exposed to 1N H₂SO₄ without inhibitor.

| Mild steel in 1N H₂SO₄ | Possible groups | Mild steel in 1N H₂SO₄ with RD(F) extract |
|------------------------|----------------|------------------------------------------|
| 2291.98                | Nitrile        | 2316.09                                  |
| Isocyanate –N=C=O      |                | 2268.84                                  |
| Aliphatic cyanoide/nitrile |            |                                          |
| Transition metal carbonyl |            |                                          |
| Fluoro alkanes         | 2046.10        |
| Skeletal C-C vibration | 1056.80        |
| Primary alcohol C-O (S) |                |                                          |
| 1015.34                | Aromatic CH in plane bend |                  |
| Aromatic fluoro compounds |                        |                                          |
| C-F(S)                 |                |                                          |
| 554.43                 | Aliphatic iodo compounds |                 |
|                        | C-I (S)        |                                          |

2790.49
2655.50
2592.82
2519.54
2458.80
2393.23
2333.45
2268.20
2239.91
2116.49

N-H Ammonium ions
Multiple broad peaks

2491.58
2413.48
2393.23
2354.66
2335.37

Nitrile
Cyanoate OCN, C-OCN
Isocyanate –N=C=O asy (S)

2333.45
2268.20
2239.91
2116.49

C≡C terminal alkynes
GH alkynes

707.75

C-H (b) of aromatic
Gs C-H out of plane bend
Aliphatic chloro compounds
C-Cl (S)
3.4.1. Analysis of FTIR spectra

FTIR spectra of mild steel treated with 1N HCl / H$_2$SO$_4$ without and with RD flower extract displayed in Figure 7a and 7b and 8a and 8b, showed either a decrease in the transmittance or disappearance of some of the above said bands, giving a strong evidence for the interaction between the metal and the functional groups such as OH, NH$_2$ and C=O leading to the formation of film of large surface coverage which serves as a barrier between the corrosive acid medium and the metal thereby inhibiting corrosion and also revealing the fact that *Musa acuminata* Red Dacca flower nutrients can absorb on the metal surface on the basis of donor-acceptor interactions between lone-pair electrons of N and the vacant d-orbital of Fe substrate (Deng 2011a,b).

5. CONCLUSION

Qualitative analysis of *Musa acuminata* Red Decca flower extract showed presence of alkaloids, saponins, tannins, flavonoids, terpenoids, coumarins, phenols and steroids. Corrosion of mild steel in 1N HCl / H$_2$SO$_4$ acid medium was significantly reduced upon the additions of RD flower extract. Inhibition efficiency increased with increasing concentration of inhibitor. Maximum inhibitor efficiency was observed at an optimum concentration of 2.5% v/v. The flower extract of RD showed maximum efficiency of 99.40% in 1N HCl at 5 hours of immersion. The flower extract of RD showed maximum efficiency of 96.99% in 1N H$_2$SO$_4$ at 7 hours of immersion. RD (F) extract showed better inhibitive effect in 1N HCl when compared to H$_2$SO$_4$. Whereas RD (F) had better inhibitive effect spread throughout the various concentrations from 0.1 to 2.5% v/v in HCl medium. All the results of the present study indicate that the extracts *Red Decca* flower in 1N HCl / H$_2$SO$_4$ acid can be used as corrosion inhibitors for mild steel. Further, as these extracts are environmentally friendly, they can be considered as green corrosion inhibitors.

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