Anti-corrosive effect of Cassia alata leaves extract on Mild steel in 1.0N Hydrochloric acid

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ABSTRACT
The inhibition effect of Cassia alata leaves extract on corrosion of mild steel in 1N HCl was investigated through mass loss measurements with various time and temperature. The observed result indicated that the corrosion inhibition efficiency and degree of surface coverage were increased with increase of inhibitor concentration and temperature. The thermodynamic parameters (E_a, ΔH_ads, ΔG_ads, ΔS_ads) were evaluated for corrosion inhibition process which suggests that the adsorption is endothermic, spontaneous and chemisorptions and also the inhibitor follows Langmuir adsorption isotherm. The protective film formed on metal surface was analyzed using spectroscopic studies viz, UV, FT-IR and EDX techniques.

KEYWORDS: Mild steel, Corrosion, Cassia alata leaves, Mass loss, Adsorption isotherm
INTRODUCTION

Mild steel is the material of choice almost all the field in Worldwide due to its low cost and easy availability. It has been extensively used under different condition in chemical and allied industries in handling alkaline, acid and salt solution. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate the corrosion. One of the best way of protecting mild steel from corrosion is the use of inhibitors [1]. But the use of chemical inhibitor has been found to be more expensive, toxic, non bio-degradable and harmful to living things. Hence there is a big problem for researchers to search the non-toxic, eco-friendly corrosion inhibitors. Recent years, several green inhibitors have been used for the prevention of corrosion by most of the investigators. Few examples are *Allium Cepa* [2], *Eucalyptus globulus* [3], *Phyllanthus amarus* [4], bitter leaf powder [5], Carob seed oil [6], *Bacopa monnieri* [7], *Citrullus Vulgaris* peel [8], *Albizia lebbeck* seed [9], *Hibiscus Esculenta* leaves [10], *Jatropha curcas* [11], *Eugenia Jambolana* [12]. In continuous of our research work, our present investigation is an anti-corrosive effect of *Cassia alata* leaves on mild steel in 1N Hydrochloric acid have been investigated with various period of contact and temperature using the mass loss measurements and the corrosion product on metal surface is analysed by UV, FT-IR, EDX spectral studies.

EXPERIMENTAL

Specimen preparation

Mild steel specimen were mechanically pressed to cut different coupons, each of dimension exactly 20cm² (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desiccator and used throughout our present study.

Preparation of *Cassia alata* leaves (CAL) extract

Freshly available *Cassia alata* leaves were dried well, grinded and soaked in required alcohol for about 48hrs, and then filtered, followed by evaporation in order to remove the excess of alcohol completely and the pure plant alcoholic extract was collected. From this extract the different concentration (0-1000ppm) of stock solution was prepared and used throughout the present investigation.

Mass loss measurement

In mass loss measurement, the specimen of mild steel is immersed exactly in 100ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after 24 to 360hrs at room temperature and one hour at the temperature range of 303K to 323K. From this observed data, the corrosion rate (mmpy), percentage of inhibition efficiency (%I.E) and surface coverage (θ) was calculated using the following formulae (1-3).

\[
\text{Corrosion Rate mmpy} = \frac{87.6 \times W}{D A T}
\]  
\[
\% \text{IE} = \frac{W_1 - W_2}{W_1} \times 100
\]  
\[
\text{θ} = \frac{W_1 - W_2}{W_1}
\]

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm³), A = Area of specimen (cm²), T = time in hours.

SURFACE CHARACTERIZATION

The predominant elements present in the corrosion products was recorded by an EDX detector using a model Oxford Instrument Model - INCA Penta xFET. The stretching frequency of functional groups in the corrosion product was analysed by FT-IR spectrum using the model Jasco/Japan. The absorption maximum of the corrosion product was analysed by UV spectra using the model Jasco V670.

RESULTS AND DISCUSSION

Table 1 reflects that the variation of corrosion parameters with concentration of CAL extract on mild steel at different period of contact in 1N Hydrochloric acid. It revealed that the corrosion rate was decreased gradually with the addition of inhibitor. The maximum of 73.62% inhibition efficiency was achieved at 1000 ppm of inhibitor concentration after 360 hrs exposure time. The almost greater than 73% of surface coverage (θ) was achieved due to the co-ordination between the mild steel metal and the hetero atom (oxygen, nitrogen) present in the inhibitor.
Table 1: Variation of corrosion parameters with Concentration of CAL extract on mild steel at different period of contact in 1N Hydrochloric acid

| Concentration of inhibitor (ppm) | 24hrs | 72hrs | 120hrs | 168hrs | 216hrs | 360hrs |
|----------------------------------|-------|-------|--------|--------|--------|--------|
|                                  | C.R   | %I.E  | C.R    | %I.E   | C.R    | %I.E   | C.R    | %I.E   | C.R    | %I.E   |
| 0                                | 5.3635| ---   | 3.1113 | ---    | 2.3405 | ---    | 2.2987 | ---    | 2.1615 | ---    |
| 10                               | 4.1097| 23.3  | 2.3451 | 24.6   | 1.5185 | 35.1   | 1.2804 | 44.2   | 0.9668 | 55.2   |
| 50                               | 3.7615| 34.9  | 2.2445 | 27.8   | 1.4674 | 37.3   | 1.2074 | 47.4   | 0.8422 | 61.0   |
| 100                              | 3.5989| 32.9  | 1.8575 | 40.3   | 1.4489 | 38.0   | 1.1278 | 50.9   | 0.7809 | 63.8   |
| 500                              | 3.4828| 35.0  | 1.6718 | 46.2   | 1.4135 | 39.6   | 1.1046 | 51.9   | 0.7493 | 65.3   |
| 1000                             | 3.3203| 38.0  | 1.1919 | 61.6   | 1.3560 | 42.0   | 1.0348 | 54.9   | 0.7367 | 65.9   |

Variation of corrosion parameters with various concentration of CAL extract on mild steel at different temperature in 1N Hydrochloric acid is shown in Table-2. As can be seen from Table-2 that the corrosion rate was decreased and the percentage of inhibition efficiency increased with increase of inhibitor concentration with rise in temperature from 303 to 323K. It suggested that the adsorbed layer retards the corrosion rate when rise in temperature from 303 to 323K. The maximum of 75.00% inhibition efficiency was achieved at 323K. The value of inhibition efficiency was increased with rise in temperature. Thus, the inhibitor efficiencies were temperature dependent and it being chemically adsorbed at all temperatures. This was due to the adsorption of active molecules on the metal surface is higher than the desorption process.

Table 2: Variation of corrosion parameters with Concentration of CAL extract on mild steel at different temperature in 1N Hydrochloric acid

| Temperature (K) | Concentration of inhibitor (ppm) | Mass loss (mg) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|-----------------|---------------------------------|----------------|------------------------|---------------------------|
| 303             | 0                               | 372            | 207.29                 | --                        |
|                 | 10                              | 211            | 117.58                 | 43.27                     |
|                 | 50                              | 200            | 111.45                 | 46.23                     |
|                 | 100                             | 183            | 101.97                 | 50.80                     |
|                 | 500                             | 147            | 081.92                 | 60.48                     |
|                 | 1000                            | 135            | 075.23                 | 63.70                     |
| 313             | 0                               | 502            | 279.74                 | --                        |
|                 | 10                              | 289            | 161.04                 | 42.43                     |
|                 | 50                              | 200            | 111.45                 | 60.15                     |
|                 | 100                             | 187            | 104.20                 | 62.74                     |
|                 | 500                             | 175            | 097.52                 | 65.13                     |
|                 | 1000                            | 152            | 084.70                 | 69.72                     |
| 323             | 0                               | 572            | 318.74                 | --                        |
|                 | 10                              | 298            | 166.06                 | 47.90                     |
|                 | 50                              | 208            | 115.90                 | 63.63                     |
|                 | 100                             | 198            | 110.33                 | 65.38                     |
|                 | 500                             | 147            | 094.73                 | 70.27                     |
|                 | 1000                            | 135            | 079.68                 | 75.00                     |
**Adsorption isotherm**

The adsorption process was influenced by the chemical structures of molecule present in CAL, the distribution of charge in molecule, the nature and surface charge of metal and the type of aggressive media. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. In those cases, the plot of log C versus log C/θ yield a straight line, clearly proving that the adsorption of the used inhibitors from 1N HCl solutions on the metal surface obeys the Langmuir adsorption isotherm (Fig.1) which is represented by equation (7).

\[ \log C/\theta = \log C - \log K \]

Where \( \theta \) is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant from which the free energy of adsorption (\( \Delta G_{ads} \)) is calculated by the following Equation (8) and the corresponding values are shown in Table-2. The negative values of \( \Delta G_{ads} \) suggested that the adsorption of CAL extract onto the metal surface is a spontaneous process and the adsorbed layer is more stable.

\[ \Delta G_{ads} = -2.303 RT \log (55.5 K) \]

Where R is the gas constant, T is the temperature. The above adsorption isotherm reveals that there is no interaction between the adsorbate and adsorbent.

![Figure 1 Langmuir isotherm for the adsorption of CAL inhibitor on mild steel in 1N Hydrochloric acid.](image)

**Table 3: Langmuir adsorption parameters for the adsorption of CAL extract on Mild steel in 1N Hydrochloric acid**

| Adsorption Isotherms | Temperature (Kelvin) | \( \Delta G_{ads} \) (kJ/mol) |
|----------------------|----------------------|-----------------------------|
| Langmuir             | 303                  | -1.914                      |
|                      | 313                  | -2.222                      |
|                      | 323                  | -2.522                      |

**Thermodynamics parameters**

A plot of log CR vs. 1000/T gave straight lines as shown in Fig.2. The apparent activation energy (Ea) was calculated by using following relationship.

\[ CR= Aexp \left( -E_a/RT \right) \]

\[ \log CR= \log A- E_a/RT \]

Where Ea is the apparent activation energy for the corrosion of mild steel in 1N HCl solution, R the gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of Ea obtained from the slope of the lines are given in Table-4.
An alternative formula of the Arrhenius equation is the transition state equation

$$CR = RT/Nh \ exp (\Delta S/R) \ exp (-\Delta H/RT)$$

where h is the Planck's constant, N the Avogadro's number, $\Delta S$ the entropy of activation, and $\Delta H$ the enthalpy of activation. A plot of log (CR/T) vs. $1000/T$ should give a straight line (Fig.3) with a slope of $(-\Delta H/R)$ and an intercept of $\log(R/Nh) + (\Delta S/R)$, from which the values of $\Delta S$ and $\Delta H$ were calculated and listed in Table 4. The data shows that the thermodynamic parameters (Ea and $\Delta H$) of the corrosion of mild steel in 1N HCl solution in the presence of the inhibitors are lower than those in the free acid solution indicating less energy barrier for the reaction in the presence of the inhibitor is attained. The positive value of enthalpy of activation reflects the endothermic nature of metal dissolution process meaning that dissolution of metal is difficult. The increase of $\Delta S$ is generally interpreted by increase in disorder taking place on going from reactants to the activated complex [13]

Table 4: Thermodynamic parameters for mild steel in 1N HCl solution obtained from weight loss measurements.

| S.No | Concentration of CAL (ppm) | Ea (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) |
|------|-----------------------------|-------------------|-----------------------------|-------------------------------|
| 1    | 0                           | 7.63142           | 6.5022                      | 8.5795                       |
| 2    | 10                          | 6.15111           | 5.0219                      | 9.4771                       |
| 3    | 50                          | 0.68416           | 0.4450                      | 11.8856                      |
| 4    | 100                         | 1.38511           | 0.2559                      | 11.6249                      |
| 5    | 500                         | 2.60444           | 1.4752                      | 11.1840                      |
| 6    | 1000                        | 1.04889           | 0.8230                      | 11.8972                      |
Figure 3 The relation between log(CR/T) and 1/T for different concentrations of CAL extract

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UV spectrum:

Fig. 4 UV spectrum of ethanolic extract of CAL (a), the corrosion product on mild steel in 1N HCl in the presence of CAL extract (b).

FT-IR analysis

Fig. 5 and 6 reflects that the FT-IR spectrum of the ethanolic extract of CAL inhibitor and the corrosion product on mild steel in the presence of inhibitor in 1N Hydrochloric acid. On comparing these spectra, the prominent peak is shifted from 3317.34 to 3355.88 cm\(^{-1}\) for –OH group, the frequency at 1119.93 cm\(^{-1}\) is attributed to –C-N stretching in amine is shifted to 1149.38 cm\(^{-1}\) indicates that the bonding between metal and inhibitor takes place through amino group. Thus the FT-IR spectra support the fact that the corrosion inhibition of CAL inhibitor on mild steel in 1N Hydrochloric acid may be the adsorption of active molecule in the inhibitor and surface of the metal.
EDX spectrum

EDX spectroscopy was used to determine the elements present on the mild steel surface in the absence and presence of inhibitor. Fig. 7 and 8 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CAL extract in 1N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum may concluded that the existence of chlorine due to the formation of metal chloride and in addition to this, spectrum consists of iron, silicon, carbon which is the part of composition of mild steel. However, in the presence of the optimum concentrations of the inhibitors, nitrogen and oxygen atoms are found to be present in the corrosion product on the metal surface. It clearly indicates that these hetero atoms present in the inhibitor molecules may involve the complex formation with metal atom during the adsorption process and prevent the further dissolution of metal against corrosion.
CONCLUSION

On the basis of the above results, it can be seen that *Cassia alata* leaves is a good inhibitor for mild steel in 1N HCl. The inhibition efficiency of CAL attains a maximum value of 73.62%. This inhibition effect increases with the increase of inhibitor concentration. The inhibition efficiency of CAL is dependent on temperature. CAL shows an adsorption on the metal surface according to the Langmuir adsorption isotherm model. The value of activation energy ($E_a$), enthalpy of adsorption ($\Delta H_{ad}$) and free energy changes ($\Delta G_{ad}$) indicates that the adsorption of inhibitor on metal surface follows chemical, endothermic and spontaneous process respectively. The corrosion product over the surface of mild steel is characterized by UV, FT-IR and EDX studies also confirm protective film completely shielded the entire metal surface and reduce the further dissolution of metal against corrosion.

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