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# Inhibitive Action of *Ailanthus excelsa* Roxb. Extract on the Corrosion of Mild Steel in Hydrochloric Acid Medium

**R. Vasantha Jothi*, R. Saratha, D. Senthil Vadivu**

*Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, Tamil Nadu, India.*

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***ABSTRACT***

*The inhibitive action of Ailanthus excelsa Roxb. (AEL) on mild steel (MS) corrosion in 1.0 M hydrochloric acid was studied using the chemical method. The effect of temperature on the corrosion behavior of MS in 1.0M HCl with the addition of plant extracts was studied in the temperature range of 308-333 ± 1 K, and inhibition efficiencies up to 98% for AEL were obtained. Adsorption of AEL on the MS surface was found to obey Langmuir adsorption isotherm. Free energy of adsorption ($\Delta G_{ads}$) calculated from the temperature studies revealed the possibility of both physisorption and chemisorption. Scanning electron microscopy images confirm the formation of protective film on the metal surface by adsorption of inhibitor which offers protection against acid attack.*

**Key words:** *Ailanthus excelsa Roxb, Corrosion inhibitor, Mild steel, Weight loss method, Adsorption isotherm, Scanning electron microscopy.*

## 1. INTRODUCTION

Among the various metals, mild steel (MS) is frequently used in different industrial sectors due to its low cost and high mechanical strength [1]. However, it is easily prone to corrosion in aqueous environment, particularly in acidic solution which is widely used in industrial process such as pickling, industrial acid cleaning, acid descaling, and oil well acidizing process [2,3]. Hydrochloric acid is commonly employed in pickling process as it is economical, efficient when compared to other mineral acids. Therefore, the corrosion of steel in such environments and its inhibition is considered to be highly a complex process. Use of Inhibitor is one of the methods to protect metals against corrosion, particularly in acid media.

Organic compounds containing heteroatoms have been reported as effective corrosion inhibitors because they can easily adsorb on the metal surface through their π bonds, non-bonding electrons, conjugated double bonds, and aromatic rings which act as adsorption center [4-6]. Many of these organic inhibitors are synthetic chemicals which are very expensive and toxic to living creatures and the environment.

The recent trend is focusing toward the use of environment-friendly inhibitors, as they are inexpensive, non-toxic, biodegradable, and readily available in abundance. Various parts such as seeds, fruits, leaves, flowers, stem, and bark [7,8] have been used as corrosion inhibitors.

Intensive number of scientific studies has been dedicated to the inhibitive action of many plant extracts on the corrosion of MS in acidic medium, showing that these extracts could serve as good corrosion inhibitors: The cited extracts include *Bryophyllum pinnatum* [9], *Psidium guajava* [10], *Pancratium foetidum* [11], *Ficus asperifolia* [12], *Pennisetum purpureum* [13], *Mentha piperita and Mentha pulegium* [14], *Senna italica*[15], *Strawberry* [16], A*calypha indica* [17], *Ruta graveolens* [18], *Aspilia africana* [19], *Maesobatrya barteri* [20].

*Ailanthus excelsa* Roxb (AEL) belongs to Simaroubaceae family (common name: Tree of heaven, perumaram) authenticated by Botanical Survey of India, Tamil Nadu Agricultural University, Coimbatore. The leaves contain glycosides, phenol, saponins, tannins, and flavonoids [21,22]. In the present study, the inhibition potential of AEL in 1.0M HCl was studied using weight loss method by varying inhibitor concentration, time of immersion, and temperature. From the weight loss data, thermodynamic and kinetic parameters were evaluated.

*Corresponding Author:
*E-mail: vachu.jo@gmail.com*

## 2. EXPERIMENTAL

### *2.1. Specimen and Inhibitor Preparation*

Sheets of cold-rolled MS purchased from the local market of 2 mm thickness were mechanically cut into 5 cm × 1 cm and were used for the study. Elemental analysis of the MS specimen was done on optical emission spectrometer DV4 model, and it reports the following composition C-0.005%, Mn-0.172%, Si-0.22%, P-0.045%, and S-0.042%, and rest is iron. Before all measurements, the surface of the MS was abraded using emery papers (grades 400-800) washed with distilled water and degreased with acetone and finally dried by storing in desiccators. The acid solution was prepared by the dilution of analytical grade 37% HCl with double-distilled water using the standard procedure.

Fresh leaves (2 kg) of AEL were collected from foothills of Palani, shade-dried for a week, and powdered. The extract was prepared by refluxing 5 g of dried powder of AEL for 3 h at 333K in 100 ml of 1.0M HCl. The solution was cooled to room temperature, filtered, and then used to prepare the desired concentration by dilution with 1.0 M HCl.

### *2.2. Chemical Techniques (Weight Loss Method)*

MS specimens abraded with a series of emery paper, washed with distilled water degreased with ethanol, and dried in acetone were used for weight loss measurements. After accurately weighing, three similar MS specimens were completely immersed in an open beaker containing 100 mL of 1.0 M HCl with and without different concentrations of inhibitor at different temperatures (308, 313, 323, and 333K) for 1 h of immersion. Then, the MS was taken out and immersed in a beaker containing saturated solution of sodium bicarbonate to remove residual acid washed with distilled water dried, and the mass of the MS specimens was determined using a digital balance. Inhibitor concentration starting from 0.01 to 0.5% v/v was used. Similarly, the experiment was carried out for different periods of immersion, say 1 h, 3 h, 7 h, 24 h, and 48 h at varying concentrations for 3 h of immersion at room temperature. Inhibition efficiency (% IE) and corrosion rate (CR mils per year) were calculated using the following equations:

$$\%IE = W_o\text{-}W_i/W_o \times 100 \quad (1)$$

Where $W_o$ and $W_i$ are the weight loss of MS specimens in the absence and presence of inhibitor, respectively.

$$CR_{mpy} = 5.34\times10^5\times\Delta W/DAt \quad (2)$$

ΔW is the difference in the weight loss (g) of the specimens in the absence and presence of inhibitor, D is the density of the MS specimen (7.89 g/cm$^3$), A is the area of the specimen (inch$^2$), and t is the exposure time (h).

### *2.3. Surface Morphological Analysis by Scanning Electron Microscope (SEM)*

The surface morphology of the corroded and inhibited specimen of MS was analyzed using SEM (Zeiss-Oxford Instruments X-act 51-ADD0058). The images were shot after immersing the samples for 24 h at room temperature in 1.0M HCl without and with the presence of 0.5 (% V/V) of AEL extract.

## 3. RESULTS AND DISCUSSION

### *3.1. Chemical Techniques (Weight Loss Method)*

#### *3.1.1. Effect of immersion period and inhibitor concentration*

Table 1 shows the calculated values of % IE and CR of the inhibitor at different concentrations on MS surface for different immersion periods for 1 h, 3 h, 7 h, 24 h, and 48 h. The data clearly show that the % IE increases with increasing concentration of inhibitor from 0.01% to 0.5% V/V and CR decreases. The decrease in the CR with increasing the AEL extract concentration clearly indicates the simple adsorption mechanism of the inhibitor [23]. The maximum IE for 1 h was 81% and gradually increases up to 89% for 3 h immersion, and a maximum efficiency of 98% was attained for 48 h of immersion for 0.5% V/V of AEL, which was found to be the optimum concentration. The increase of % IE with increasing of inhibitor concentration indicates the strong adsorption of the inhibitor molecules on the MS surface in 1.0M HCl medium.

### *3.2. Effect of Temperature*

Temperature studies are considered to be an important parameter for evaluating thermodynamic parameters. The % IE and CR obtained for different temperatures from 303K-333K are listed in Table 2. The data clearly show that as the temperature increases, % IE increases and the CR is decreased. The maximum IE was found to be 97% at 0.5% V/V at 333K, which indicated that AEL extract was found to be a good inhibitor in 1.0M HCl medium and it was stable even at a higher temperature. The relationship between CR and temperature (T) was expressed by Arrhenius equation (3).

$$\text{Log CR} = Ae^{-Ea/RT} \quad (3)$$

Where A is the frequency factor, $E_a$ is the activation energy, R is the gas constant (R = 8.314 J/mol/K), and T is the absolute temperature. Straight lines were obtained by plotting log CR against 1/T as shown in Figure 1 for the corrosion of MS in the absence and presence of different concentrations of AEL. The slope of the line is equal to $-E_a/2.303R$ from which $E_a$ can be calculated and presented in Table 3. $E_a$ values in the presence of AEL extract were found to decrease when compared to the blank (1.0M HCl) indicating the strong adsorption of the extract on to the metal surface, i.e., chemisorptions [24].

### *3.3. Adsorption Isotherm*

Adsorption isotherm plays a vital role in predicting the nature of interaction between the inhibitor molecule and metal surface and type of the adsorption process. The

**Table 1:** CR of MS in 1.0M HCl, with and without AEL extract and the corresponding IE from weight loss measurements at 308K for different immersion periods.

| Concentration of AEL (% v/v) | 1 h | | 3 h | | 7 h | | 24 h | | 48 h | |
|---|---|---|---|---|---|---|---|---|---|---|
| | IE (%) | CR (mpy) | IE (%) | CR (mpy) | IE (%) | CR (mpy) | IE (%) | CR (mpy) | IE (%) | CR (mpy) |
| Blank | - | 765 | - | 565 | - | 638 | - | 810 | - | 878 |
| 0.01 | 63 | 280 | 80 | 115 | 91 | 76 | 91 | 43 | 97 | 30 |
| 0.05 | 73 | 205 | 84 | 90 | 93 | 54 | 93 | 27 | 98 | 21 |
| 0.1 | 74 | 197 | 85 | 87 | 94 | 50 | 94 | 25 | 98 | 16 |
| 0.5 | 81 | 144 | 89 | 64 | 96 | 34 | 96 | 19 | 98 | 14 |

**Table 2:** CR and IE for various concentrations of AEL extract for the corrosion of MS in 1.0M HCl at different temperatures.

| Concentration of AEL (%v/v) | 303 K | | 313 K | | 323K | | 333K | |
|---|---|---|---|---|---|---|---|---|
| | IE (%) | CR (mpy) | IE (%) | CR (mpy) | IE (%) | CR (mpy) | IE (%) | CR (mpy) |
| Blank | - | 765 | - | 1189 | - | 4216 | - | 11375 |
| 0.01 | 63 | 280 | 74 | 310 | 79 | 900 | 80 | 1949 |
| 0.05 | 73 | 205 | 83 | 201 | 91 | 371 | 93 | 795 |
| 0.1 | 74 | 197 | 85 | 179 | 92 | 341 | 95 | 546 |
| 0.5 | 81 | 144 | 90 | 122 | 94 | 236 | 97 | 385 |

**Table 3:** Thermodynamic parameters for adsorption of AEL extract on MS in 1M HCl at different temperatures.

| Concentration of AEL (%v/v) | $E_a$ KJ/mol | $-\Delta G_{ads}$ KJ/mol | | | | $-\Delta H_{ads}$ KJ/mol | $\Delta S_{ads}$ KJ/mol/K |
|---|---|---|---|---|---|---|---|
| | | 303K | 313K | 323K | 333K | | |
| Blank | 84.28 | - | - | - | - | | |
| 0.01 | 56.88 | 23.09 | 25.26 | 27.17 | 27.17 | 19.32 | 0.14 |
| 0.05 | 39.11 | 20.26 | 22.23 | 24.39 | 24.39 | 23.45 | 0.14 |
| 0.1 | 30.53 | 18.78 | 20.94 | 23.21 | 23.21 | 27.94 | 0.15 |
| 0.5 | 29.90 | 15.1 | 17.91 | 20.43 | 20.43 | 40.29 | 0.18 |

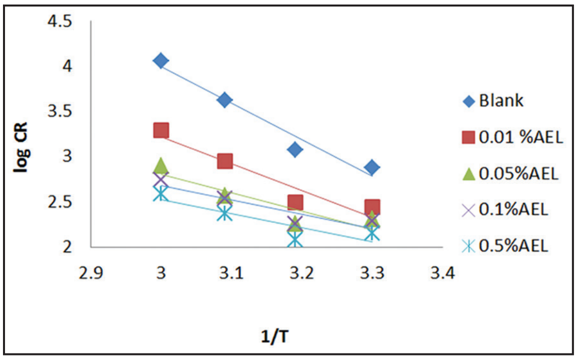


**Figure 1:** Log CR versus 1/T curves for MS dissolution in 1.0M HCl in the absence and presence of *Ailanthus excelsa* Roxb extract.

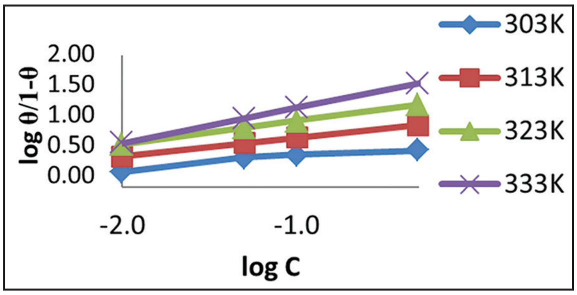


**Figure 2:** Langmuir isotherm for adsorption of AEL extract on the MS surface in 1.0 M HCl at different temperatures.

values of the degree of surface coverage (θ) obtained from % IE for different concentrations of inhibitor were evaluated from weight loss measurements at 303 K-333K for 1 h immersion period in 1.0M HCl. Various adsorption isotherms were tested, and Langmuir isotherm was found to be the best fit and is represented by the following equation 4.

$$\theta/1-\theta = K_{ads}C \qquad (4)$$

Where C is the concentration of inhibitor, $K_{ads}$ is the equilibrium constant of adsorption on MS surface, and θ is the surface coverage given by the equation 5.

$$\theta = \%IE/100 \quad (5)$$

The Langmuir isotherm is obtained by plotting log $\theta/1-\theta$ versus log C as shown in Figure 2. The free energy of adsorption ($\Delta G_{ads}$) and the equilibrium constant K at various concentrations of inhibitor for different temperatures were calculated using the following equation 6.

$$\Delta G_{ads} = -RT\ln 55.5\ K \quad (6)$$

Where $K=\theta/C_{inh}(1-\theta)$, R is the gas constant, T is the temperature, and the constant value of 55.5 represents the concentration of water in solution. In general, the value of $\Delta G_{ads}$ less negative than −20 KJ/mol indicates physisorption and the value more negative than −40KJ/mol signifies chemisorption [25]. Table 3 shows the calculated values of $\Delta G_{ads}$ and is found to be <−40 KJ/mol, indicating the inhibition process as physisorption.

The heat of adsorption ($\Delta H_{ads}$) and entropy of adsorption ($\Delta S_{ads}$) were calculated by plotting $\Delta G_{ads}$ against T. The slope of this straight line gives $\Delta H_{ads}$ value, and the intercept gives $\Delta S_{ads}$. The calculated thermodynamic parameters are listed in Table 3. The negative value of $\Delta H_{ads}$ indicates the adsorption of inhibitor molecules onto the metal surface is exothermic reaction. The change in entropy ($\Delta S_{ads}$) was found to be greater than zero (0.14-0.18) which indicates that the reaction is irreversible. Even though the $\Delta G_{ads}$ values indicate that the adsorption process is physisorption, the other thermodynamic parameters show that the process is chemisorption, which indicates the adsorption process to be physisorption followed by chemisorption [26].

### *3.4. SEM Studies*

Figure 3 represents the SEM obtained for the MS surface 1.0M solution with and without the inhibitor, after exposure for 1 day of immersion. The SEM micrographs revealed that the surface morphology was strongly damaged in the absence of inhibitor, but in the presence of 0.5 (% v/v) of the inhibitor, the damage was considerably reduced and the surface became smooth, which confirmed the high efficiency of AEL extract at this concentration.

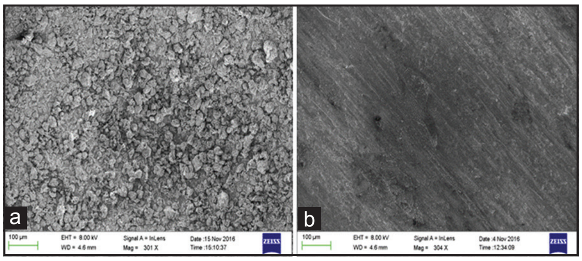


**Figure 3:** (a and b) Scanning electron microscopy micrographs for MS in the absence and presence of 0.5 (%v/v) of AEL extract.

## 4. CONCLUSION

The plant extract (AEL) acted as an effective corrosion inhibitor for MS in 1.0 M HCl. The IE of the inhibitor was increased when the concentration of inhibitor was increased. At the concentration of 0.5% V/V, the plant extract showed a maximum inhibition of 90% for AEL in 1.0M HCl. Langmuir adsorption isotherm was obeyed. Thermodynamic adsorption parameters ($\Delta H_{ads}$ and $\Delta G_{ads}$) revealed that the adsorption of inhibitor onto the MS surface was spontaneous and endothermic. SEM images provided information of protective film formation on the MS surface. As a final point, the plant extract of AEL is easily available, cost effective, and environmentally friendly green inhibitor for 1.0M HCl corrosion of MS.

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***Bibliographical Sketch**

R.Vasantha jothi had completed her schooling in Immaculate convent in the year 1998.She qualified her under graduation (B.Sc Chemistry) in the year 2001 at P.S.G.R Krishnammal College for women ,Coimbatore and worked as a primary school teacher for about 2 years. In the year 2005 she began her post graduation in Kongunadu Arts and Science College, Coimbatore.Her PG project specialized in Lithium ion batteries and was carried out at Central Electrochemical Research Institute, and Karaikudi.She pursued her M.Phil in the area of Synthetic organic Chemistry. She has work experience as an Assistant professor for a period of 3 years from 2010-2013.In the year 2014 ,she registered for her doctoral research programme in the Department of Chemistry ,Avinashilingam Institute for Home Science and Higher Education for women, Coimbatore -43,Tamilnadu ,India. Her area of research is Corrosion Science and Electrochemistry. She has presented about 5 papers in National/International conferences and has published one review paper. She aims to accomplish a teaching career in chemical sciences