

## *Tectona grandis* Leaf Extract as Environmental Friendly Corrosion Inhibitor for SS304 Stainless Steel in Hydrochloric Acid

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The corrosion inhibitory effects of *Tectona grandis* (teak) leaves extract, for stainless steel 304 (SS304) in 2 M hydrochloric acid was investigated using gravimetric technique and scanning electron microscopy (SEM). The gravimetric results showed that the corrosion rate decreases with increase in inhibitor concentration. The maximum inhibition efficiency of 65% for teak leaves was obtained at 1000 ppm extract concentration. It was found that the inhibition efficiency increased with temperature. The studies revealed that the teak leaf extract acts as a mixed type inhibitor. Adsorption of the inhibitor molecules on the surface of stainless steel followed comprehensive adsorption.

**Keywords:** Corrosion, Green Inhibitor, Adsorption, Isotherm, Stainless Steel

### Introduction

Stainless steel 304 (SS304) is widely used in industries because of its corrosion resistant behaviour provided by the formation of chromium oxyhydroxide on its surface when coming into contact with aggressive environments<sup>1</sup>. However, this protective layer becomes less effective in the control of corrosion in the medium containing halogens<sup>1</sup>. Many synthetic organic heterocyclic compounds containing molecules such as nitrogen, sulphur, oxygen or compounds containing multiple bonds as adsorption centres are claimed to act as good corrosion prevention agents for stainless steel corrosion in acidic medium containing halogens<sup>2-13</sup>. However, the toxicity of such chemical compounds has raised environmental concerns<sup>3</sup>. Recently studies on the use plant materials as inexpensive green corrosion inhibitor has gained importance. Extracts of fennel seed, bee wax propolis, *Ricinus communis* and *Salvia officinalis* were reported to have good anticorrosion properties for SS304 in acidic medium<sup>9-12</sup>. The present work investigates the use of *Tectona grandis* (teak) leaves extract as corrosion inhibitor for SS304 in 2 mol L<sup>-1</sup> hydrochloric acid (HCl). The extent of corrosion was studied using weight loss measurements at various inhibitor concentrations and temperature. The morphology of the surface was

studied using scanning electron microscopy (SEM). The chemical composition of the surface was measured by energy dispersive X-ray analysis (EDAX). The chemical composition of the solution before and after immersion of the stainless steel specimen in different medium was studied using atomic absorption spectroscopy (AAS).

### Experimental

*Tectona grandis* leaves were ground to fine powder after drying. Teak leaves powder was then soaked in 500 mL ethanol for 24 h which was then refluxed for 5 h between 50 °C and 55 °C and then concentrated using vacuum evaporator. Stainless steel grade 304 was used as the material for corrosion investigation in 2 M HCl. The SS304 coupons used for weight loss studies were of 1 cm radius (*r*) and 0.5 cm thickness. Cleaned and pre-weighed SS304 coupons were immersed in beakers containing 50 mL of 2 M HCl with and without inhibitor. The difference in the weight obtained for the coupon before and after the immersion for a specified period was noted down. The corrosion inhibition efficiency and corrosion rate was calculated from the weight loss of the coupons in the presence and the absence of inhibitor reported in detail elsewhere<sup>10</sup>. The solution remaining after immersion of the SS304 coupons were analysed for iron and chromium content using atomic absorption spectroscopy (AAS). The samples for SEM, EDAX were prepared by immersion of the cleaned coupons

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in 2 M hydrochloric acid solution with and without 1000 ppm inhibitor.

## Results and Discussion

### Effect of inhibitor concentration

The effect of inhibitor concentration on inhibition efficiency (IE) for SS304 in 2 M HCl with 4 h immersion period is shown in Figure 1. It can be observed from the Figure 1 that the inhibition efficiency increases with increase in the inhibitor concentration up to 1000 ppm. The observed increase in the inhibition effect with inhibitor concentration up to 1000 ppm could be attributed to the adsorption of the extract molecules on the SS304 surface<sup>13</sup>.

Table 1 shows the concentration of iron and chromium in the test solution with and without 1000 ppm inhibitor extract after different immersion periods analyzed using AAS. It is clearly seen from the Table 1 the extract is effective in controlling the corrosion of SS304 in 2 M HCl and effectively controls the release of iron into the solution but provides moderate control over the release of chromium.

### Effect of temperature and thermodynamic activation parameters

Table 2 shows the results of the corrosion studies conducted at various temperatures for a SS304

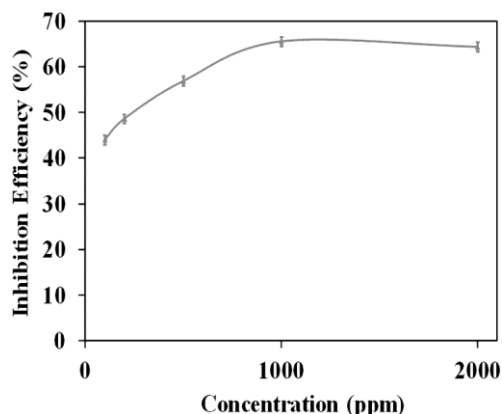


Fig. 1 — Inhibition efficiency at different inhibitor concentrations for SS304 in 2 M HCl with 4 h immersion period.

Table 1 — AAS analysis of 2 M HCl solution after immersion of stainless steel specimen with and without 1000 ppm extract.

| Exposure time<br>(h) | Uninhibited<br>(ppm) |    | Inhibited<br>(ppm) |    |
|----------------------|----------------------|----|--------------------|----|
|                      | Fe                   | Cr | Fe                 | Cr |
| 4                    | 100                  | 19 | 14                 | 11 |
| 8                    | 208                  | 28 | 19                 | 20 |
| 12                   | 258                  | 28 | 50                 | 19 |
| 16                   | 325                  | 47 | 116                | 30 |

coupon in the presence and absence of 1000 ppm inhibitor for an hour of immersion period. It is seen from the Table 2 that the IE drops with temperature till 40 °C but increases in the temperature range from 40 °C to 75 °C. The increase in IE with temperature could be due to physisorption or specific interaction between the SS304 surface and the inhibitor molecules<sup>14</sup>. It could also be due to changing mode of adsorption- physisorption at lower temperature and chemisorption at higher temperatures<sup>10</sup>. Further, chemical changes taking place in the inhibitor molecules leads to an increase in the electron density at the adsorption centers resulting in increased IE<sup>13</sup>. The activation energy ( $E_a$ ) for the system in the presence and the absence of inhibitor was calculated using the Arrhenius equation. According to this equation,  $\log (CR)$  is the sum of two terms,  $\frac{-E_a}{2.303RT}$  and Arrhenius pre-exponential factor ( $A$ )<sup>11</sup>. The Arrhenius plot of  $\log (CR)$  versus  $(1/T)$  is shown in Figure 2(a) and the corresponding values of  $E_a$  are shown in Table 3 show that the  $E_a$  are lowered in the presence of inhibitor. Though the decrease in  $E_a$  with the addition of inhibitor is reported to be an indication of chemisorption, it is believed to occur when the molecules are neutral<sup>10,15</sup>. Hence in the presence of ions, the dominating physical adsorption can be explained as the reason for drop in  $E_a$  with the addition of inhibitor<sup>15</sup>. When  $E_{a, \text{inh}} < E_{a, \text{blank}}$  and the  $A$  value in the absence of inhibitor is higher when compared to the inhibited case, smaller number of more active sites which remain unoccupied take part in the corrosion process<sup>14,15</sup>. An  $E_a$  between 40 kJ mol<sup>-1</sup> and 80 kJ mol<sup>-1</sup> represent comprehensive adsorption which makes it clear that the present system follows the same<sup>13</sup>. The enthalpy of activation ( $\Delta H_a$ ) and entropy of activation ( $\Delta S_a$ ) for the system were calculated using the transition state equation 1 from the results of the weight loss experiments at different temperatures with and without 1000 ppm inhibitor<sup>13</sup>.

Table 2 — Effect of temperature on the corrosion of SS304 with and without 1000 ppm extract in 2 M HCl for 1 h immersion period

| Temperature<br>(°C) | CR Uninhibited<br>(mm y <sup>-1</sup> ) | CR Inhibited<br>(mm y <sup>-1</sup> ) | $\eta$<br>(%) |
|---------------------|-----------------------------------------|---------------------------------------|---------------|
| 28                  | 1.5                                     | 0.9                                   | 41.5          |
| 40                  | 2.8                                     | 2.0                                   | 27.2          |
| 50                  | 5.6                                     | 3.2                                   | 42.6          |
| 60                  | 10.9                                    | 5.7                                   | 48.1          |
| 70                  | 19.9                                    | 8.6                                   | 57.0          |
| 75                  | 31.4                                    | 13.4                                  | 57.4          |

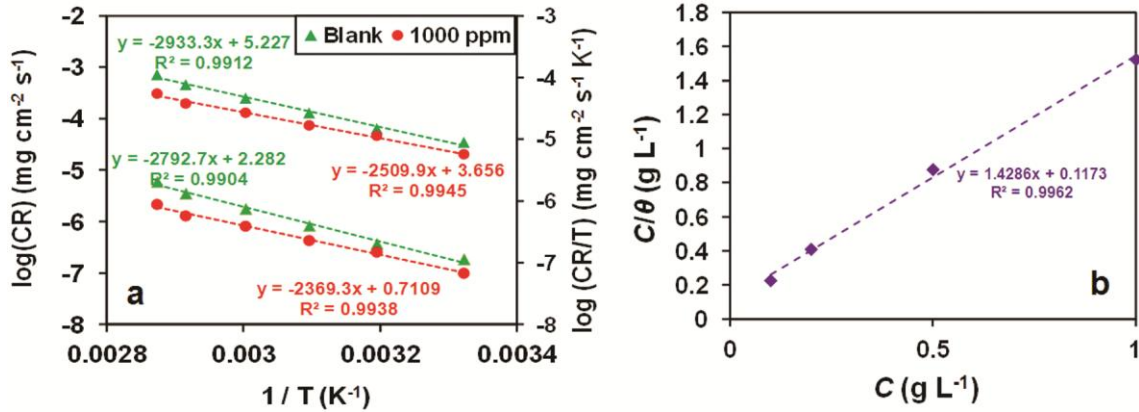


Fig. 2 — Thermodynamic and adsorption isotherm plots for SS304. a. Thermodynamic plots for SS304, immersion period: 1h b. Langmuir adsorption isotherm plot for SS304 with 1000 ppm inhibitor at room temperature. The dotted lines represent straight line fit.

Table 3 — Thermodynamic and Langmuir adsorption isotherm parameters for SS304 in 2 M HCl with and without 1000 ppm inhibitor

| Thermodynamic parameters                           |       |                      |
|----------------------------------------------------|-------|----------------------|
| Parameter                                          | Blank | Inhibitor (1000 ppm) |
| $\Delta H_a$ ( $\text{kJ mol}^{-1}$ )              | 53    | 45                   |
| $E_a$ ( $\text{kJ mol}^{-1}$ )                     | 56    | 48                   |
| $\Delta S_a$ ( $\text{J mol}^{-1} \text{K}^{-1}$ ) | -153  | -183                 |
| Langmuir Isotherm                                  |       |                      |
| $k_{\text{ads}}$ ( $\text{L g}^{-1}$ )             |       | 10.8                 |
| $\Delta G^0$ ( $\text{kJ mol}^{-1}$ )              |       | -23                  |

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{2.303R} - \frac{\Delta H_a}{2.303RT} \quad \dots (1)$$

In equation 1,  $R$  is the universal gas constant,  $N$  is the Avogadro's number and  $h$  is the Planck's constant. A plot of  $\log(CR/T)$  versus  $1/T$  is shown in Figure 2(a). The values of  $\Delta H_a$  and  $\Delta S_a$  are shown in Table 3. A positive  $\Delta H_a$  refers to the endothermic nature of the dissolution process. Large negative  $\Delta S_a$  suggests that the activated complex in the rate determining step characterizes an association rather than a dissociation step, which is an indication of a decrease in disordering on going from reactants to the activated complex<sup>16</sup>.

#### Adsorption isotherm

The surface coverage ( $\theta$ ) of the adsorbed molecules was determined by dividing the inhibition efficiency values of the weight loss with 100<sup>17</sup>. The results obtained for  $\theta$  were analyzed using Langmuir isotherm. Langmuir adsorption isotherm can be given by equation 2<sup>13</sup>.

$$\frac{C}{\theta} = \frac{1}{k_{\text{ads}}} + C \quad \dots (2)$$

where  $C$  is the concentration of the inhibitor in  $\text{g L}^{-1}$ ,  $k_{\text{ads}}$  is the equilibrium constant of the adsorption

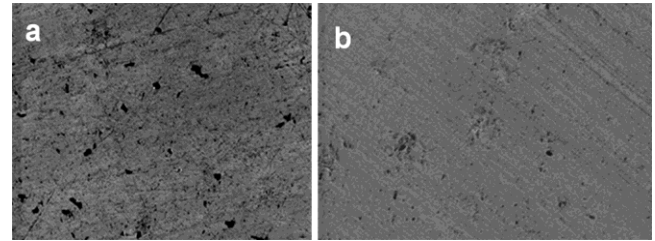


Fig. 3 — SEM images of the SS304 samples immersed in 2 M HCl after 4 h immersion. a. blank and b. inhibited.

process. Figure 2(b) shows the plots of Langmuir adsorption isotherm obtained using gravimetric techniques. The standard free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) for the system can be calculated using equation 3<sup>13</sup>.

$$\Delta G_{\text{ads}}^0 = -RT \ln k_{\text{ads}} \times \rho_w \quad \dots (3)$$

In equation 3,  $R$  is the universal gas constant in  $\text{J mol}^{-1} \text{K}^{-1}$ ,  $T$  is absolute temperature in K,  $\rho_w$  is the density of water in  $\text{g L}^{-1}$ . The  $k_{\text{ads}}$  and  $\Delta G_{\text{ads}}^0$  values are presented in Table 3. A  $\Delta G_{\text{ads}}^0$  value more negative than  $-40 \text{ kJ mol}^{-1}$  is an indication of chemisorption and those below  $-20 \text{ kJ mol}^{-1}$  as physisorption process. In the present study the  $\Delta G_{\text{ads}}^0$  values are in the range from  $-23 \text{ kJ mol}^{-1}$  which is a mixture of both physisorption and chemisorption processes<sup>13</sup>.

#### Scanning electron microscopy

Figure 3 (a,b) show the SEM images of the SS304 samples after immersion for 4 h in  $2 \text{ mol L}^{-1}$  HCl without and with inhibitor respectively. It is clearly seen that the surface of the SS304 samples without inhibitor shows the occurrence of pitting corrosion to a higher extent than inhibited one.

### Conclusion

The effect of *T. grandis* leaf extract on the corrosion of SS304 in 2 M HCl was investigated. It was seen that the maximum inhibition efficiency of 65% was obtained for 1000 ppm inhibitor concentration. The inhibition efficiency drops with increase in immersion temperature. Temperature studies indicate that *T. grandis* extract provides better inhibition against corrosion phenomena at higher temperatures. *T. grandis* extract was found to act as a mixed type inhibitor. Adsorption of the extract molecules on the SS304 surface was found to follow comprehensive adsorption.

### References

- 1 Abdallah M, Rhodanine azosulpha drugs as corrosion inhibitors for corrosion of 304 stainless steel in hydrochloric acid solution, *Corros Sci*, **44** (2002) 717-728.
- 2 Refaey S A M, Taha F & Abd El-Malak A M, Inhibition of stainless steel pitting corrosion in acidic medium by 2-mercaptobenzoxazole, *Appl Surf Sci*, **236** (2004) 175-185.
- 3 Soltani N, Tavakkoli N, Khayatkashani M, Jalali M R & Mosavizade A, Green approach to corrosion inhibition of 304 stainless steel in hydrochloric acid solution by the extract of *Salvia officinalis* leaves, *Corros Sci*, **62** (2012) 122-135.
- 4 Hosseini S M A & Salari M, Corrosion inhibition of stainless steel 302 by 1-methyl-3-pyridine-2-Y1-thiourea in acidic media, *Indian J Chem Technol*, **16** (2009) 480-485.
- 5 Sharma M, Chawla J & Singh G, Cetyltrimethylammonium bromide as corrosion inhibitor for mild steel in acidic medium, *Indian J Chem Technol*, **16** (2009) 339-343.
- 6 Vishwanatham S & Haldar N, Corrosion inhibition of N80 steel in Hydrochloric acid by phenol derivatives, *Indian J Chem Technol*, **14** (2007) 501-506.
- 7 Fouda A S & Elattar K M, Corrosion inhibition of carbon steel by new enamionitrile derivatives in HCl solution, *J Sci Ind Res*, **71** (2012) 690-698.
- 8 Fouda A S, Rashwan S M & Abo-Mosallam H A, Aqueous extract of coriander seeds as green corrosion inhibitor for 304 stainless steel in hydrochloric acid solutions, *J Korean Chem Soc*, **58** (2014) 25-32.
- 9 Gapsari F, Seonoko R, Suprpto A & Suprpto W, Bee wax propolis extract as eco-friendly corrosion inhibitors for 304SS in sulfuric acid, *Int J Corros*, 567202 (2015) 1-10.
- 10 Victoria S N, Prasad R & Manivannan R, *Psidium guajava* leaf extract as green corrosion inhibitor for mild steel in phosphoric acid, *Int J Electrochem Sci*, **10** (2015) 2220-2238.
- 11 El Maghraby A A & Soror T Y, Efficient cationic surfactant as corrosion inhibitor for carbon steel in hydrochloric acid solutions, *Adv Appl Sci Res*, **1** (2010) 156-168.
- 12 Sathiyathan R A L, Maruthamuthu S, Selvanayagam M, Mohanan S & Palaniswamy N, Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves, *Indian J Chem Technol*, **12** (2005) 356-360.
- 13 Chidiebere M A, Oguzie E E, Liu L, Li Y & Wang F, Ascorbic acid as corrosion inhibitor for Q235 mild steel in acidic environments, *J Ind Eng Chem*, **26** (2015) 182-192.
- 14 Ibrahim M A M, Messali M, Moussa Z, Alzahrani A Y, Alamry S N & Hammouti B, Corrosion inhibition of carbon steel by imidazolium and pyridinium cations ionic liquids in acidic environment, *Port Electrochim Acta*, **29** (2011) 375-389.
- 15 Noor E A & Al-Moubaraki A H, Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/1-methyl-4[4'(-X)-styryl pyridinium iodides/ hydrochloric acid systems, *Mater Chem Phys*, **110** (2008) 145-154.
- 16 Solmaz R, Kardaş G, Çulha M, Yazıcı B & Erbil M, Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media, *Electrochim Acta*, **53** (2008) 5941-5952.
- 17 Fu J J, Li S N, Cao L H, Wang Y, Yan L H & Lu L D, L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution, *J Mater Sci*, **45** (2010) 979-986.