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# Influence of wrightia tinctoria leaves on the corrosion of brass in acid medium

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**Abstract**
The influence of Wrightia tinctoria leaves toward the corrosion of brass in 1.0N HCl was investigated by using mass loss measurement with various period of contact and temperature. The observed results suggest that the percentage of inhibition efficiency is enhanced with increase of inhibitor concentration and temperature. When the temperature increases the % of inhibition efficiency also increases may reveals that the adsorption of inhibitor on the metal surface takes place through chemisorptions process. The thermodynamic parameter such as Ea, ΔS, $Q_{ads}$ ΔHads and $\Delta G_{ads}$ suggests that the adsorption may be exothermic and spontaneous process. It was found out that the adsorption of WTL inhibitor follows Langmuir adsorption isotherm. The corrosion product may also be confirmed by the spectral studies such as UV, FT-IR, and the film formation by SEM image.

**Keywords:** Brass, Mass Loss, Corrosion, Wrightia tinctoria leaves, Adsorption

## 1. Introduction

Copper is easily combined with many metals. It is combined with various percentage of zinc to form different types of brass, which has a higher corrosion resistance and is easy to manufacture. The proportions of zinc and copper can be varied to create a range of brasses with varying properties which include strength, machinability, ductility, wear resistance, hardness, colour, antimicrobial, electrical and thermal conductivity, and corrosion resistance. Various types of brass respond to corrosion effect in different ways in different environments. Continuous investigation in this regard is therefore an absolute necessity to ensure safe, reliable and functional utilisation and to mitigate ugly application consequences. Moreover, brass is harder and solid material, but its exposure in acid media leads to corrosion [1] for this reason, the corrosion behavior of these metals has attracted more awareness of several investigators. In recent years many alternative ecofriendly corrosion inhibitors have been developed. Plant extracts are environmentally ecofriendly, bio-degradable, non-toxic, plenty and potentially low cost. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors". These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds and containing heteroatom like oxygen, nitrogen and sulphur. Recently many investigators using plants like Prunus cerasus [2], Un-caria gambir[3], Raphia hookeri [4], Black Pepper [5], Leb-beckSeed [6], Eugenia Jambolana seed [7], Cassia alata leaves[8] Jatropha curcas [9], Pyrus pyrifolia fruit peel [10] Tridax procumbens [11], coffee ground [12], Gossipium hirsutum [13], Ginseng Root [14], Isertia coccinea [15] mimusops elengi leaves [16] Sauropus androgynus leaves [17] kingiodendron pinnatum leaves [18] *Gymenma Sylvestre* [19] have been found effective corrosion inhibitors for Brass. In continuous of our research work, the present investigation is the corrosion behaviour of *Wrightia tinctoria leaves* on Brass in 1.0N Hydrochloric acid have been investigated with various periods of contact and temperature using the mass loss measurements. Also the corrosion product on the metal surface is analysed by UV, FT-IR, and surface morphology by SEM.

## 2. Materials and methods

### 2.1 Specimen preparation

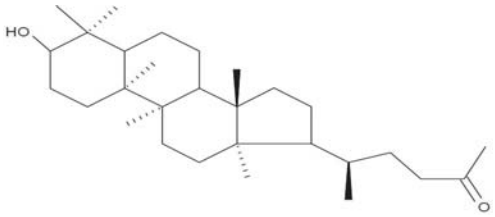
Brass specimen were mechanically pressed cut to form different coupons, each of dimension exactly $20cm^2$ (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desicator for the use of all our present study.

### 2.2 Preparation of *Wrightia Tinctoria Leaves (*WTL) Extract

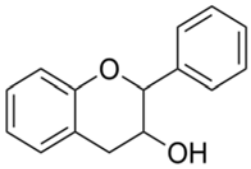
About 2 Kg of *Wrightia Tinctoria* leaves (WTL) was collected from in and around Western Ghats and then dried under shadow for 5 to 10 days. Then it is grained well and finely powdered, exactly 200g of this fine powder was taken in a 500ml round bottom flask and a required quantity of ethyl alcohol was added to cover the fine powder completely, and left it for 48 hrs. Then the resulting paste was refluxed for about 48 hrs, the extract was collected and the excess of alcohol was removed by the distillation process. The obtained paste was boiled with little amount of activated charcoal to remove impurities, the pure plant extract was collected and stored.

### 2.3 Properties of *Wrightia tinctoria leaf*

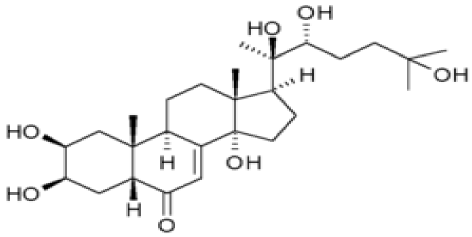
*Wrightia tinctoria* belongs to *Appocynaceae family* and it is an annual herbaceous climbing plant with a long history of traditional medicinal uses in many countries, especially in tropical and subtropical regions. The common Names are *vetpalai*. The peel extract of this plant is used to regulate thyroid function and glucose metabolism. The main phytochemicals constituents present in this plant is wrightial, flavonoids, alkaloids, saponins, and triterpenes. A few importance structures are shown below.



Wrightial



Flavan-3-ol (Flavanoid)



20-Hydroxyecdysone (Saponin)

**Fig 1:** Chemical structure of the main active compounds present in Wrightia tinctoria leaves

### 2.4 Mass loss measurement

In the mass loss measurements on Brass in triplicate were completely immersed in 100ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured 313K to 333K. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6 \times W}{DAT} \quad \ldots (1)$$

Where,

mmpy = millimoles per year,

W = Mass loss (mg), D = Density (gm/cm$^3$),

A = Area of specimen (cm$^2$), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\% \text{ IE} = \frac{W_1 - W_2}{W_1} \times 100 \quad \ldots (2)$$

$$\theta = \frac{W_1 - W_2}{W_1} \quad \ldots (3)$$

Where $W_1$ and $W_2$ are the corrosion rates in the absence and presence of the inhibitor respectively.

### 2.5 Adsorption studies

#### 2.5.1 Activation energy

The activation energy ($E_a$) for the corrosion of metals in the presence and absence of inhibitors in 1.0N Hydrochloric acid, natural sea water environment was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4).

$$CR = A\exp(-E_a/RT) \quad \ldots (4)$$

$$\log(CR_2/CR_1) = E_a/2.303\, R\,(1/T_1 - 1/T_2) \quad \ldots (5)$$

Where $CR_1$ and $CR_2$ are the corrosion rate at the temperature $T_1$ (313K) and $T_2$ (333K) respectively.

#### 2.5.2 Heat of adsorption

The heat of adsorption on the surface of various metals in the presence of plant extract in 1.0N Hydrochloric acid, Natural sea water environment is calculated by the following equation (6).

$$Q_{ads} = 2.303R[\log(\theta_2/1 - \theta_2) - \log(\theta_1/1 - \theta_1)] x (T_2T_1/T_2 - T_1) \quad \ldots (6)$$

Where R is the gas constant, $\theta_1$and $\theta_2$ are the degree of surface coverage at temperatures $T_1$ and $T_2$ respectively.

#### 2.5.3 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm can be expressed by the following Equation-4.10 is given below.

$$\log C/\theta = \log C - \log K \quad \ldots (7)$$

Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface.

#### 2.5.4 Free energy of adsorption

The equilibrium constant of adsorption of various plant extract on the surface of Brass is related to the free energy of adsorption $\Delta G_{ads}$ by equation (8).

$$\Delta G_{ads} = -2.303\, RT \log(55.5\, K) \quad \ldots (8)$$

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption

## 3. Result and Discussion

### 3.1 Mass loss measurements

Dissolution behavior of Brass in 1.0N Hydrochloric acid environment containing in the presence and absence of WTL extract with various exposure times (24to 360 hrs) are shown in Table-1. The observed values are clearly indicates that in the presence of WTL extract the value of corrosion rate decreased from 0.8989 to 0.1463mmpy for 24 hrs and 0.9365 to 0.1491mmpy for 360 hrs with increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 87.08 % of inhibition efficiency is achieved even after 120 hrs exposure time. This achievement is mainly due to the presence of active phytochemical constituents present in the inhibitor molecule which is adsorbed on the metal surface and shield completely to prevent further dissolution from the aggressive media of chloride ion ($Cl^-$).

**Table 1:** The corrosion parameters of Brass in 1.0N Hydrochloric acid containing different concentration of WTL extract after 120 to 480 hours exposure time

| Conc (ppm) | Corrosion rate (mmpy) | | | | | Inhibition efficiency (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 24 hrs | 72 Hrs | 120 hrs | 240 hrs | 360 hrs | 24 Hrs | 72 hrs | 120 hrs | 240 hrs | 360 hrs |
| 0 | 0.8989 | 0.8431 | 0.8738 | 0.8968 | 0.9365 | - | - | - | - | - |
| 10 | 0.5017 | 0.5783 | 0.4222 | 0.5497 | 0.5560 | 44.18 | 31.40 | 51.67 | 38.69 | 40.62 |
| 50 | 0.4180 | 0.4250 | 0.2926 | 0.4410 | 0.4390 | 53.48 | 49.58 | 66.50 | 50.81 | 53.12 |
| 100 | 0.2717 | 0.3414 | 0.2714 | 0.3825 | 0.3693 | 69.76 | 59.50 | 68.89 | 57.34 | 60.56 |
| 500 | 0.2508 | 0.2647 | 0.2257 | 0.2738 | 0.2062 | 72.09 | 68.59 | 74.16 | 69.46 | 77.97 |
| 1000 | 0.1463 | 0.1811 | 0.1128 | 0.1400 | 0.1491 | 83.72 | 78.51 | 87.08 | 84.38 | 84.07 |

### 3.2 Temperature Studies

Dissolution behavior of Brass containing various concentration of WTL extract in 1.0N Hydrochloric acid with temperature ranges from 313K to 333K is investigated by mass loss measurement and the values are listed out in Table 2. The observed values of corrosion rate decreased from 9.5326 to 3.5120 mmpy at 313K with increase of inhibitor concentration. The percentage of inhibition efficiency is gradually increased from 63.15 to 76.62% with increase of inhibitor concentration, suggests that the absorption process is chemisorption. Also these results may cofirm that the binding between the inhibitor molecules and the metal ion in the surface.

**Table 2:** The corrosion parameters of Brass in 1.0N Hydrochloric acid containing different concentration of WTL extract at 313 to 333 K

| Conc. (ppm) | Corrosion rate (mmpy) | | | Inhibition efficiency (%) | | |
|---|---|---|---|---|---|---|
| | 313K | 323K | 333K | 313K | 323K | 333K |
| 0 | 9.5326 | 17.0584 | 38.6323 | - | - | - |
| 10 | 8.5292 | 14.0481 | 20.5704 | 10.52 | 17.64 | 46.75 |
| 50 | 7.0240 | 13.5463 | 16.0549 | 26.31 | 20.58 | 58.44 |
| 100 | 6.0206 | 10.5360 | 14.5498 | 36.84 | 38.23 | 62.33 |
| 500 | 4.5154 | 7.5257 | 12.5429 | 52.63 | 55.88 | 67.53 |
| 1000 | 3.5120 | 5.0171 | 9.0309 | 63.15 | 70.58 | 76.62 |

### 3.3 Effect of temperature

#### 3.3.1 Activation energy

The values of corrosion rate obtained from the mass loss measurement are substituted in Equation-4 and the values of activation energy ($E_a$) are presented in Table-3. The observed values are ranged from 39.136 to 26.414 kJ/mol for Brass in 1.0N Hydrochloric acid containing various concentration of inhibitor. The average value of $E_a$ obtained from the blank (39.136) is greater than that in the presence of inhibitor and indicated that there is a strong chemical adsorption bond between the WTL inhibitor molecules and the Brass surface.

**Table 3:** Calculated values of Activation energy ($E_a$) and heat of adsorption ($Q_{ads}$) of WTL extract on Brass in 1.0N Hydrochloric acid environment.

| S. No | Conc. of inhibitor (ppm) | % of I.E | | $E_a$ (KJmol$^{-1}$) | $Q_{ads}$ (KJmol$^{-1}$) |
|---|---|---|---|---|---|
| | | 30$^o$ | 60$^o$ | | |
| 1. | 0 | -- | -- | 39.136 | -- |
| 2. | 10 | 10.52 | 46.78 | 24.621 | 56.218 |
| 3. | 50 | 26.31 | 58.44 | 23.120 | 38.322 |
| 4. | 100 | 36.84 | 62.33 | 24.678 | 29.159 |
| 5. | 500 | 52.63 | 67.53 | 28.572 | 17.535 |
| 6. | 1000 | 63.15 | 76.62 | 26.414 | 18.127 |

#### 3.3.2 Heat of adsorption

The value of heat of adsorption ($Q_{ads}$) on copper in 1.0N Hydrochloric acid containing various concentration of WTL extract is calculated using Equation-6 and the values of $Q_{ads}$ are ranged from 56.218 to 18.127 kJ/mol (Table-3). These positive values are reflected that the adsorption of WTL extract on Brass is follows endothermic process.

#### 3.3.3 Adsorption studies

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study the Langmuir adsorption isotherm is investigated. The straight line observed in Fig- 2 suggest that the inhibitor follows Langmuir adsorption isotherm.

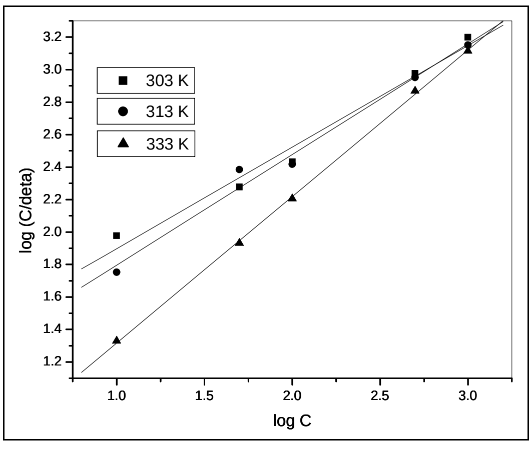



**Fig 2:** Langmuir isotherm for the adsorption of WTL inhibitor on Brass in 1.0N hydrochloric acid environment.

### 3.3.4 Free energy of adsorption

The standard free energy of adsorption ($\Delta G_{ads}$) can be calculated using the Equation- 8 and the observed negative values in Table-4 ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced.

**Table 4:** Langmuir adsorption parameters for the adsorption of WTL inhibitor on Brass in 1.0N Hydrochloric acid.

| Adsorption isotherms | Temperature (Kelvin) | Slope | K | $R^2$ | $\Delta G_{ads}$ kJ/mol |
|---|---|---|---|---|---|
| Langmuir | 303 | 0.6254 | 18.7150 | 0.9798 | -17.4775 |
| | 313 | 0.6812 | 13.0256 | 0.9847 | -17.1111 |
| | 333 | 0.9018 | 2.5989 | 0.9995 | -13.7413 |

### 3.3.5 Thermodynamics parameters

The another form of transition state equation which is derived from Arrhenius equation -4 and 9

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \quad \text{.... (9)}$$

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs. 1000/T gives a straight line (Fig- 3) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed out in Table-5. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult. The ΔS is generally interpreted with disorder which may take place on going from reactants to the activated complex

**Table 5:** Thermodynamic parameters of Brass in 1.0N HCl solution obtained from weight loss measurements.

| S. No | Concentration of WTL (ppm) | ΔH (kJ $mol^{-1}$) | ΔS (J $k^{-1}mol^{-1}$) |
|---|---|---|---|
| 1 | 0 | 15.6817 | 11.9879 |
| 2 | 10 | 9.1231 | 9.7894 |
| 3 | 50 | 8.0089 | 9.4139 |
| 4 | 100 | 9.0177 | 9.6477 |
| 5 | 500 | 10.9179 | 10.1561 |
| 6 | 1000 | 10.2565 | 9.8279 |

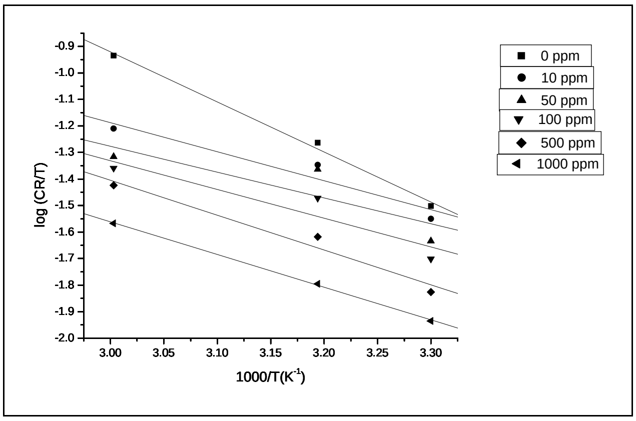



**Fig 3:** The relation between log (CR/T) and 1/T for different concentrations of WTL extract

## 4. Spectral Studies

### 4.1 UV Analysis

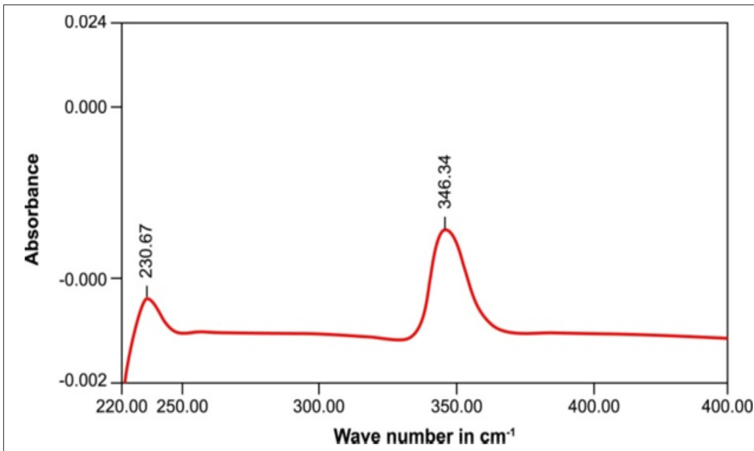



**Fig 4**

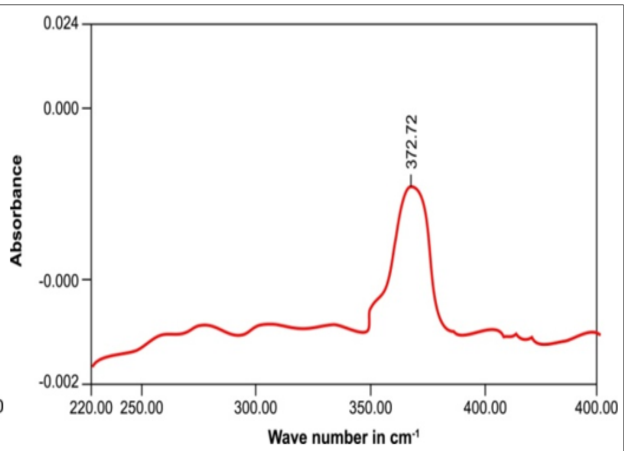



**Fig 5**

**Fig 4-5:** UV spectrum of corrosion product in the absence and presence of WTL on the brass in 1.0N HCl

Figures 4 and 5 shows that the UV visible spectrum of the corrosion product on the surface of brass in the presence and absence of WTL extract in 1.0N hydrochloric acid. In the absence of inhibitor, the UV absorption maximum of two bands around 230.67nm and 346.34nm were appeared. However in the presence of inhibitor only one peak was appeared at around 372.72 nm and shifted to higher wavelength region, indicates Bathochromic Shift? The change of adsorption band revealed that the strong co-ordination between the active group present in the inhibitor molecules and ion from the metal surface.

### 4.2 FT-IR Analysis

**FT-IR studies of WTL extract on Brass surface in 1.0 N Hydrochloric acid**

The figures-6 and 7 reflect that the FTIR spectrums of the ethanolic extract of inhibitor and the corrosion product on Brass in the presence of WTL extract in 1.0N HCL. On comparing both of these spectra the prominent peak such as, the –N-H stretching frequency for amine is shifted from 3379.05 to 3317.34 $cm^{-1}$, the C=O stretching frequency for carbonyl is shifted from 1654.81 to 1645.17 $cm^{-1}$ and the C-H stretching frequency is shifted from 1401.03 to 1388.78 $dcm^{-1}$. These results support the fact that the corrosion inhibition of WTL extract on Brass in 1.0N HCL may be prevented further dissolution of the metal.

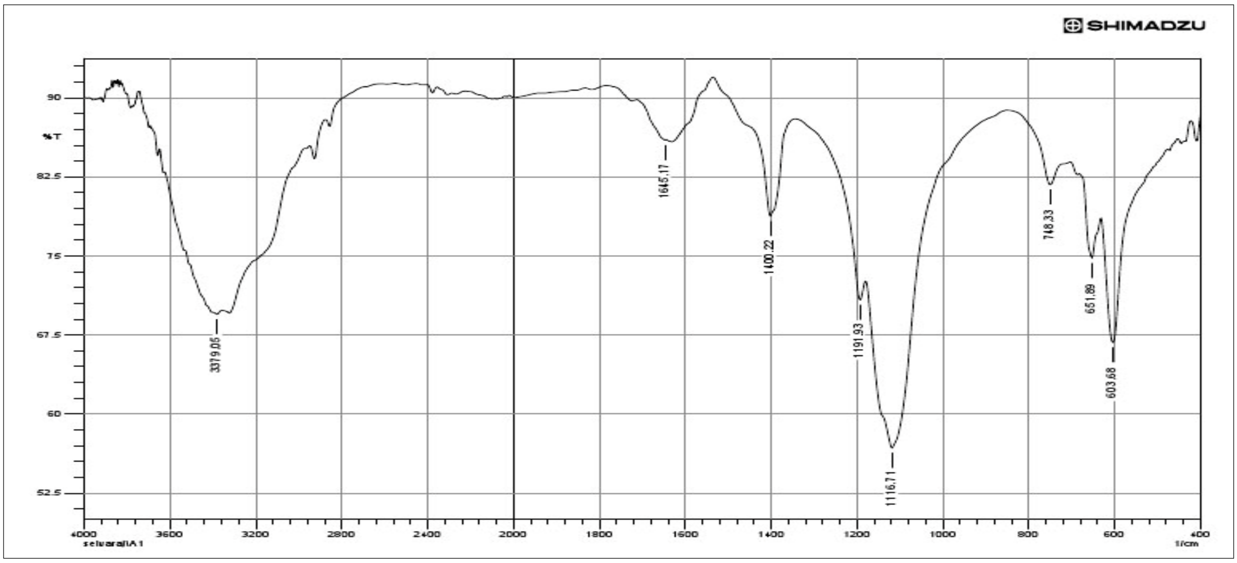



**Fig 6:** FT-IR spectrum of ethanolic extact of *wrightia Tinctoria* laeves (WTL)

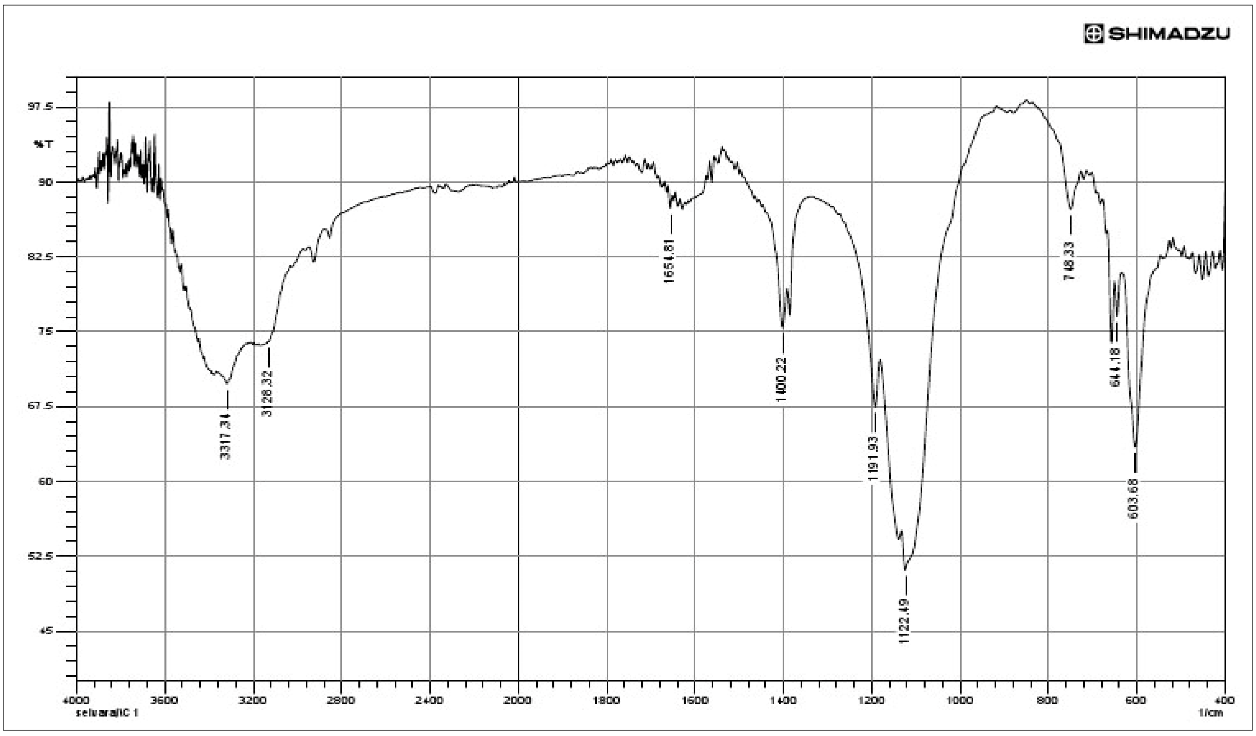



**Fig 7:** FT-IR spectrum for the corrosion product on Brass in the presence of WTL extract with 1.0N HCL

**5. SEM Analysis**

The surface morphology of Brass surface was studied by scanning electron microscopy (SEM). The Figures- 8 and 9 shows that the SEM micrographs of copper surface before and after immersion in 1.0N HCL respectively. The SEM photographs showed that the surface of metal has number of pits and cracks are visible in the surface, but in presence of inhibitor they are minimized on the metal surface. It is clearly indicates that the formation of spongy mass covered on the entire metal surface.

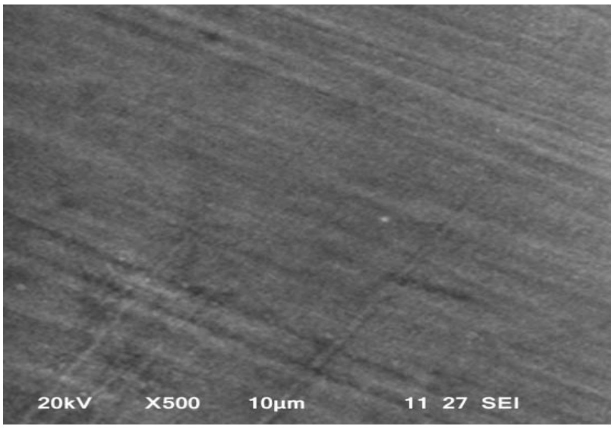



**Fig 8:** SEM image of the Brass surfaces immersed in1.0N HCL,

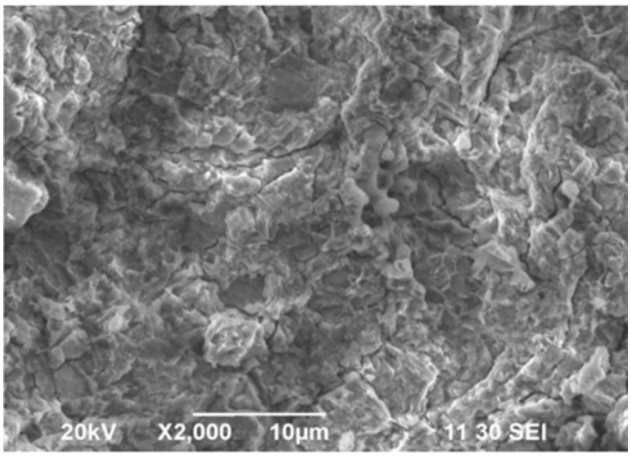



**Fig 9:** SEM Image of the brass surface immersed in1.0N HCL with WTL extract

## 6. Conclusion

Corrosion of *Wrightia tinctoria* leaves on Brass in 1.0N Hydrochloric acid is increased with increase of exposure period from 24 to 360 hours. But using WTL extract on Brass, the corrosion rate markedly reduced with increase of concentrations (0 to 1000ppm). The maximum inhibition efficiency is achieved 87.08%. It is a good inhibitor for acid environment on brass. This is due to strong bindings between the inhibitor molecule and ions from the metal surface. By temperature studies, the percentage inhibition efficiency increased with rise of temperature ranges from 313 to 333K is due to the adsorption of active inhibitor molecules on the metal surface is higher than desorption process. The maximum 76.62% inhibition efficiency is attained. It follows chemisorptions. The activation energy ($E_a$), heat of adsorption ($Q_{ads}$), Standard free energy adsorption ($\Delta G_{ads}$), enthalphy ($\Delta H$), entropy ($\Delta S$), suggests that, strong chemical bond, endothermic, spontaneous process respectively. The inhibitor obeys Langmuir adsorption isotherm. The film formation may confirm by SEM spectral studies and the corrosion products characterised both using UV and FT-IR Spectral studies.

## 7. Acknowledgements

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