# Milling tonia hortensis linin.f extract as corrosion inhibitor for mild steel in aqueous medium

## J. Rosaline Vimala[1*], A. Leema Rose[1] and S. Raja[2]

[1]*Department of Chemistry, Holy Cross College(Autonomous), Tiruchirappalli, India*
[2]*Department of Chemistry, St. Joseph's College(Autonomous), Tiruchirappalli, India*

_____

## ABSTRACT

*The inhibition efficiency of aqueous extract of milling tonia hortensis linin.F (MTHL) on the corrosion of mild steel in ground water was investigated by weight loss measurements and electrochemical studies. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained showed that the extract could serve as an effective inhibitor for the corrosion of mild steel in aqueous media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich and the thermodynamic model, were tested to clarify the nature of adsorption. Potentiodynamic Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 81% can be obtained.*

**Keywords:** Milling tonia hortensis linin.F (MTHL), Mild steel, Temkin's adsorption isotherm, Potentiodynamic polarization.

_____

## INTRODUCTION

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media[1-19]. Plant extracts constitute several organic compounds which have corrosion inhibiting abilities. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant [20-23] and its location [22]. The extracts from the leaves, seeds, heartwood, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media [20, 21, 23-36]. A summary of plants extracts used as corrosion inhibitors have recently been given in Okafor *et al*. [21] and Raja and Sethuraman [37]. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

_____

## MATERIALS AND METHODS

**Experimental**
Rectangular samples of area 4x1 cm$^2$ have been cut from a large sheet of mild steel. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with 400 grade emery papers, degreased in a solution of non-toxic detergent, washed with distilled water, dried, weighed and stored in desiccators for further use.

Ethanol extract of Milling Tonia Hortensis Linin.F was prepared by the aerial part of plant collected and dried in air and then grained. 50g of grained powder was subjected to extraction using ethanol(95%) . The solvent can be removed by boiled at constant temperature at 401˙C vacuum evaporator, finally the residue was collected. From the residue the various concentration of inhibitor solution(0.3, 0.6, 0.9, 1.2, 1.5, 1.8%v/v) was prepared. All the solutions were prepared with AR grade chemicals in double distilled water.

Polished specimens were initially weighed in an electronic balance. Weighed samples are immersed in 100 mL of the ground water without and with different concentrations of the inhibitor for various intervals of time. They are then taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed.

The parameters used for the present study are given below
1. **Time** :3 h, 6 h, 9 h, 24 h
2. **Concentration of the inhibitor** : 0.3%, 0.6%, 0.9%, 1.2%, 1.5%,1.8%(v/v)
3. **Temperatures** : (303 K , 313 K , 323 K , 333 K ) ±2 K

From the change in weight of specimens the corrosion rate was calculated using the following relationship ,

$$\text{Corrosion rate} = \frac{82.75 \times W}{A \times T \times D}$$

W = Loss in weight in mg
A = surface area of the specimen (cm$^2$)
T = Time in hrs
D = Density (7.2g/cm3)

**Potentiodynamic Polarisation Measurement**
Potentiodynamic polarisation studies were carried out using VSP primeton.100 ml of ground water without and with 1.8%(v/v)concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode was then introduced. The electrode was placed at 0.8 mV to its open circuit potential. Thus the potential was scanned at 10 mV/sec towards the anodic direction in Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants 'b$_a$' and 'b$_c$' respectively. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$I\text{ corr} = \frac{b_a \times b_c}{2.303(b_a + b_c)R_p}$$

Where, Rp is polarization resistance.

*Determination of inhibition efficiency*
By Tafel method

$$I_{corr} = \frac{I_{corr} - I_{corr(1)}}{I_{corr}} \times 100$$

where,
I$_{corr}$ is corrosion current without inhibitor
I $_{corr(1)}$ is corrosion current with inhibitor.

_____

**Impedance studies**

Impedance measurements were carried out at various corrosion potentials. An ac sine wave of 10 mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100 MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist plot. All the measurements were presented in the corrosion potential. In Impedance method, the charge transfer resistance (Rct) is obtained from the plots of Z' vs. Z'' (real part Vs imaginary part; Nyquist plot). The value $(R_p + R_s)$ corresponds to the point where the plot cuts Z axis to the point where the semicircle cuts the Z axis at high frequency. The difference gives the $R_p$ values, which were substituted in the Stern-Geary equation to get

$$I\,corr = \frac{b_a \times b_c}{2.303(b_a + b_c)R_{ct}}$$

The $b_a$ and $b_c$ values were experimentally obtained.

## RESULTS AND DISCUSSION

The inhibitor was tested for six different concentrations and their corresponding corrosiont rate data are presented in Table 1.(Figures 1,2)The addition of inhibitors increases the IE, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface. The IE is 81 % at a concentration of 1.8% v/v. The results concerned with the effect of period of immersion at various concentrations of the inhibitors on mild steel in ground water are also shown in Table 2. The IE decreases with increase in time from 24hrs to 168hrs of period of immersion.

The effect of temperature on the inhibitory action of the inhibitor was determined by mass loss method at 1.8%(v/v)concentration at different temperatures (303, 313, 323, and 333) ±2K for a fixed immersion time of 3hrs. The tabulated data (Table 3) reveal that, at a concentration of 1.8%v/v of the inhibitor the corrosion rate has increased with rise in temperatures. Though the C.R has increased with temperature for a given concentration of the inhibitor, there is irregular trend in the change of inhibition efficiency. However, the inhibitor could be effectively used at 313K and maximum efficiency being 82.14%.

Activation energy ($E_a$) and thermodynamic data, such as change in free energy($\Delta G_{ads}$), enthalpy($\Delta H$), and entropy ($\Delta S$) for mild steel in ground water in the presence and in the absence of the inhibitor was calculated are listed in the table 4. The activation energy at different temperatures and 1.8%(v/v) concentration of the inhibitor in ground water is calculated by plotting log C.R vs. 1/T(figure3 and 4). $E_a$ values for inhibited systems are lower than those for uninhibited system indicating that all the inhibitors exhibit high I.E at elevated temperatures. The range of $E_a$ is 159.55 to 22.62 kJ/mol for MTHL in ground water. The negative values of $\Delta G_{ads}$ (-12.58 to -14.22kJ) suggest the strong interaction of the inhibitors molecules whereas low value of $\Delta G_{ads}$ indicated spontaneous adsorption of inhibitors on MS surface. The negative values of $\Delta H$ (157.03 to 20.10 kJ/mol) indicate that the adsorption of inhibitor molecules is an exothermic reaction. The change in entropy was found to be greater than zero (0.1078).This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible.

The surface coverage (θ) values for different concentrations of the inhibitors in the both medium have been evaluated from the weight loss data. At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction (1- θ) reacts with acid as it does in the absence of the inhibitor.

The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage θ values are much useful to measure the adsorption characteristics. The surface coverage of an inhibitor at any concentration is calculated using the equation

$$\Theta = \frac{W_0 - W}{W_o}$$

_____

Where Wo and W are the weight loss without and with inhibitor respectively and the values   at different concentrations are presented in table 5.

The data were tested graphically to find a suitable adsorption  isotherm.  A plot of log [$\theta$/(1- $\theta$)] against log C (figure 5) shows a straight line (R>0.9) indicating that adsorption follows the Langmuir adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Plant extract contains organic compounds having polar atoms or groups which are absorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slopes values form unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of (1/y). A straight line was obtained when the surface coverage was plotted against log C for the inhibitor. This shows that the adsorption obeys a Tempkin adsorption isotherm, which is graphically represented in figure 6. The plots of log $\theta$ vs log C are shown in figure 7. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm.

The various electrochemical parameters calculated from Tafel plot (figures8a,8b) are given in Table 6. The lower corrosion current density ($I_{corr}$) values in the presence of inhibitor without causing significant changes in corrosion potential($E_{corr}$) (-765.536 to -688.833 mv) suggests that the compound is mixed type inhibitor (i.e.., inhibit both anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction. Since $b_a$ is greater than $b_c$ suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Impedance diagram (Nyquist plot) obtained for mild steel 1N HCl in the presence of various concentrations of the inhibitor is depicted in figure 9. They are perfect semicircles and this was attributed to charge transfer reaction. Impedance parameters derived from Nyquist plots are tabulated in Table 7. It can be seen that  the resistance has increased and  $C_{dl}$ values has decreased. Decrease in $C_{dl}$, which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal-solution interface.

**Table 1. Influence of concentration of inhibitor on percentage inhibition and corrosion rate.**

| S.No. | Inhibitor Concentration(v/v%) | Corrosion Rate(mpy) | Percentage Inhibition Efficiency |
|-------|------------------------------|---------------------|----------------------------------|
| 1 | Blank | 0.0980 | - |
| 2 | 0.3 | 0.0513 | 47.62 |
| 3 | 0.6 | 0.0513 | 47.62 |
| 4 | 0.9 | 0.0280 | 71.42 |
| 5 | 1.2 | 0.0233 | 76.19 |
| 6 | 1.5 | 0.0192 | 78.12 |
| 7 | 1.8 | 0.0186 | 81.0 |

**Table 2. Inhibition efficiency of mild steel in ground water in the presence of milling tonia hortesis linin.F at 303K at different time period**

| S.No. | Immersion period | Inhibitor concentration(v/v%) | Corrosion rate(mpy) | Percentage Inhibition efficiency |
|-------|------------------|-------------------------------|---------------------|----------------------------------|
| 1 | 24hours | Blank | 0.0980 | - |
|   |         | 1.8 | 0.0186 | 81.0 |
| 2 | 72 hours | Blank | 0.0544 | - |
|   |          | 1.8 | 0.0202 | 62.8 |
| 3 | 120 hours | Blank | 0.0690 | - |
|   |           | 1.8 | 0.0466 | 43.69 |
| 4 | 168 hours | Blank | 0.0793 | - |
|   |           | 1.8 | 0.0513 | 25.60 |

_____

**Table 3.  Protection Performance of Milling tonia hortesis linin.F on mild steel in ground water for 3 hrs at different temperatures**

| S. No. | Temperature (K) | Inhibitor Concentration (v/v%) | Corrosion Rate (mpy) | Percentage Inhibition Efficiency | Log C.R/T | $1/T \times 10^3$ |
|---|---|---|---|---|---|---|
| 1 | 303 | Blank | 0.0980 | - | -2.24 | |
| | | 1.8 | 0.0186 | 81.0 | -1.8 | 3.30 |
| 2 | 313 | Blank | 0.3920 | - | -1.78 | |
| | | 1.8 | 0.0700 | 82.14 | -1.4 | 3.19 |
| 3 | 323 | Blank | 0.6674 | - | -1.51 | |
| | | 1.8 | 0.5460 | 19.14 | -1.29 | 3.09 |
| 4 | 333 | Blank | 0.8774 | - | -1.23 | |
| | | 1.8 | 0.7094 | 18.8 | -0.85 | 3.00 |

**Table 4. Thermodynamic parameters for mild steel corrosion in ground water with Milling tonia hortesis linin.F**

| S.No. | $E_a$ (kJ/mol) | $-\Delta G_{ads}$ (kJ/mol) | | | | $-\Delta H$ (kJ/mol) | $\Delta S$ (J/mol) |
|---|---|---|---|---|---|---|---|
| | | 303k | 313K | 323K | 333K | | |
| Blank | 159.55 | - | - | - | - | 157.03 | - |
| 1.8 | 22.62 | 12.58 | 5.45 | 5.82 | 14.22 | 20.10 | 0.1078 |

**Table5.  Influence of concentration of MTHL on surface  coverage**

| S.No. | Inhibitor concentration (v/v%) | Log C | $\theta$ | Log $\theta$ | Log($\theta$/1-$\theta$) | Log($\theta$/C) | Log(1-$\theta$) |
|---|---|---|---|---|---|---|---|
| 1 | Blank | - | - | - | - | - | - |
| 2 | 0.3 | -0.52 | 0.47 | -0.32 | -0.05 | 0.20 | -0.27 |
| 3 | 0.6 | -0.22 | 0.47 | -0.32 | -0.05 | 0.20 | -0.27 |
| 4 | 0.9 | -0.04 | 0.71 | -0.14 | 0.38 | -0.10 | -0.53 |
| 5 | 1.2 | 0.07 | 0.76 | -0.11 | 0.50 | -0.19 | -0.61 |
| 6 | 1.5 | 0.17 | 0.80 | -0.09 | 0.60 | -0.26 | -0.69 |
| 7 | 1.8 | 0.25 | 0.80 | -0.09 | 0.60 | -0.34 | -0.69 |

**Table 6.  The corrosion parameters for mild steel in ground water with MTHL extract from polarization studies**

| S. No. | Environment | $E_{corr}$ Vs SCE (mv) | $B_c$ (mv) | $B_a$ (mv) | $I_{corr}$ ($\mu$A) |
|---|---|---|---|---|---|
| 1 | Blank | -429.261 | 154.1 | 332.2 | 1411.38 |
| 2 | inhibitor | -382.288 | 170.1 | 78.1 | 186.632 |

**Table 7. The corrosion parameters for mild steel in ground water with MTHL extract from impedance studies**

| S. No. | Environment | $R_t$(ohm) | Cdl(F) |
|---|---|---|---|
| 1 | Blank | 49.59 | 0.1597 |
| 2 | inhibitor | 124.9 | 0.0634 |

_____

**Figure 1.  Influence of concentration of milling tonia hortesis linin.F on percentage inhibition efficiency**
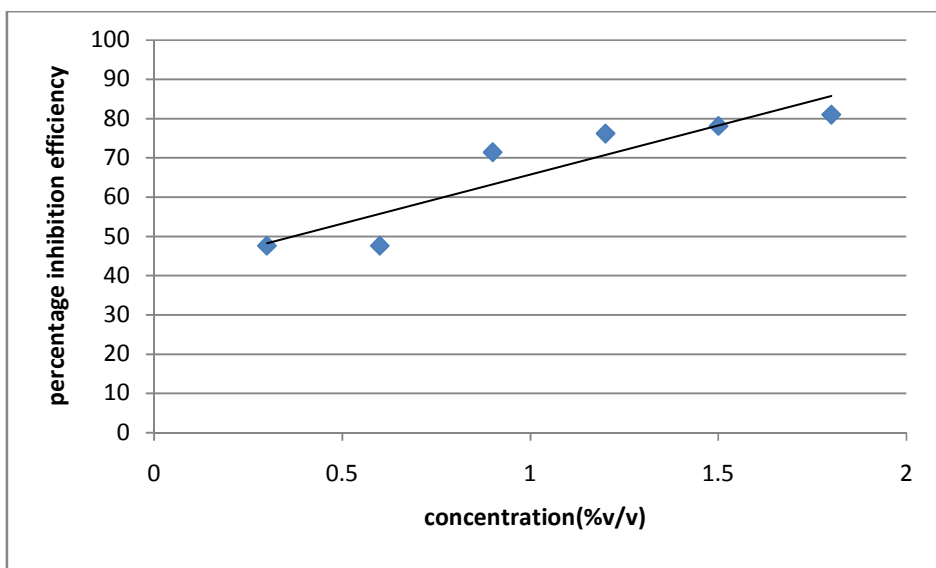


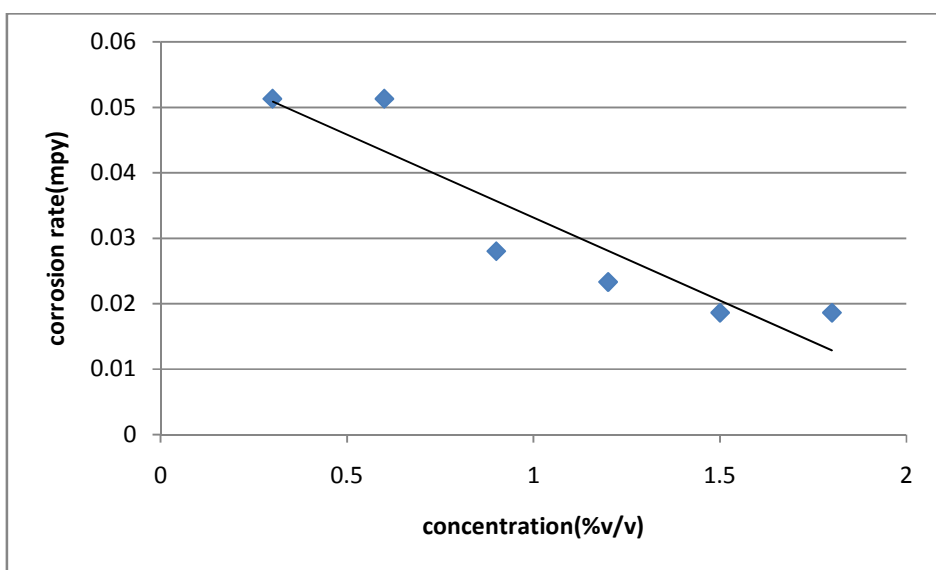**Figure 2.  Influence of concentration of milling tonia hortesis linin.F on corrosion rate**

_____

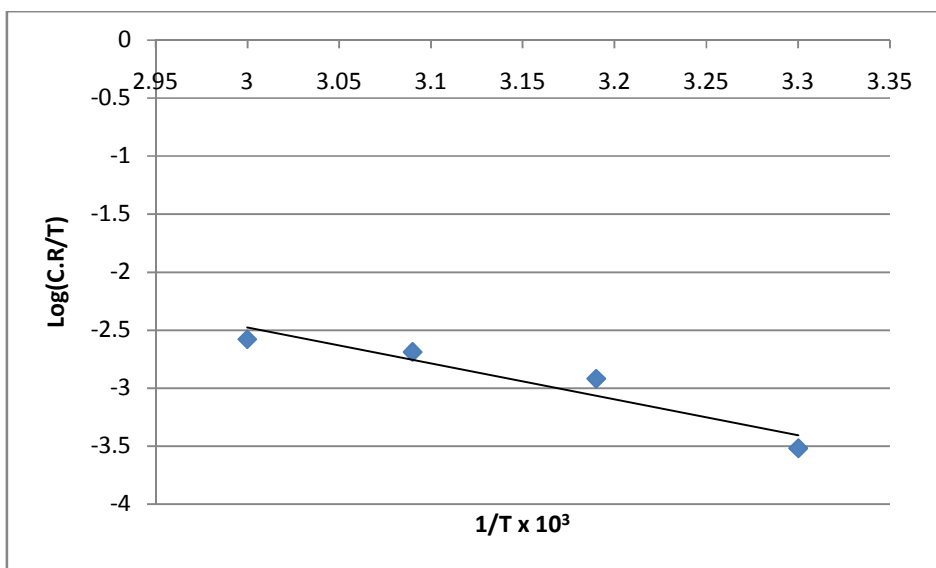**Figure 3. Arrhenius Plot for mild steel in ground water**



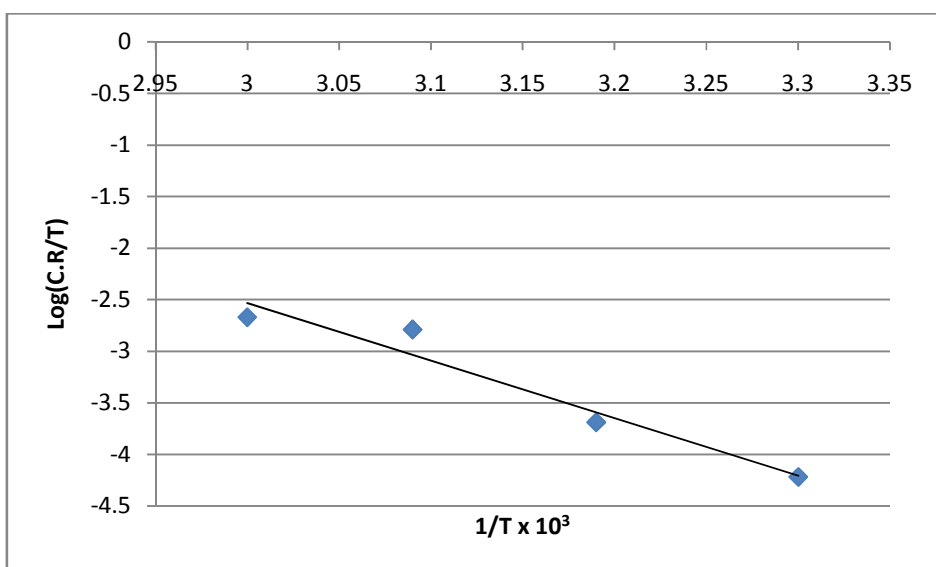**Figure 4. Arrhenius Plot for mild steel in ground water with MTHL extract**

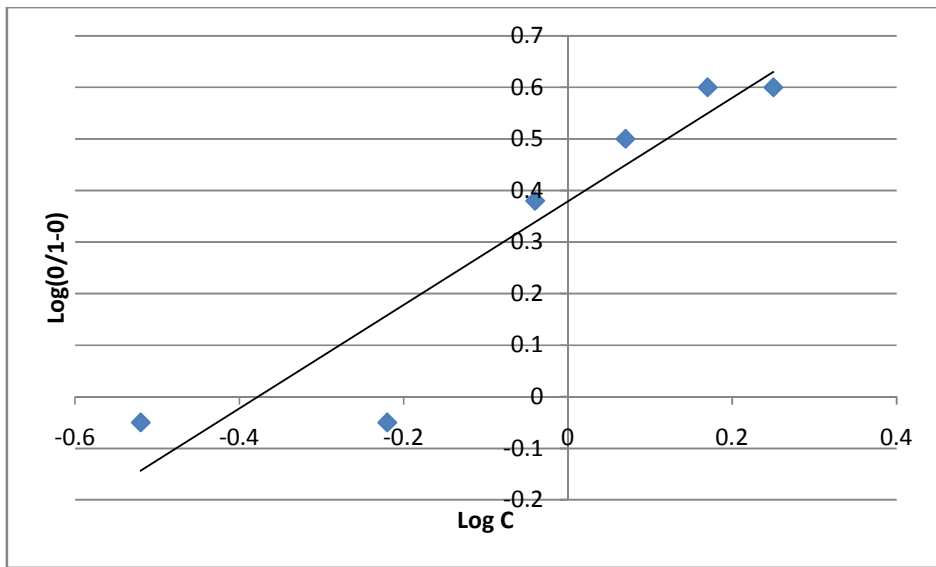**Figure 5. Langmuir adsorption isotherm for the inhibition of corrosion of mild steel by MTHL in ground water**



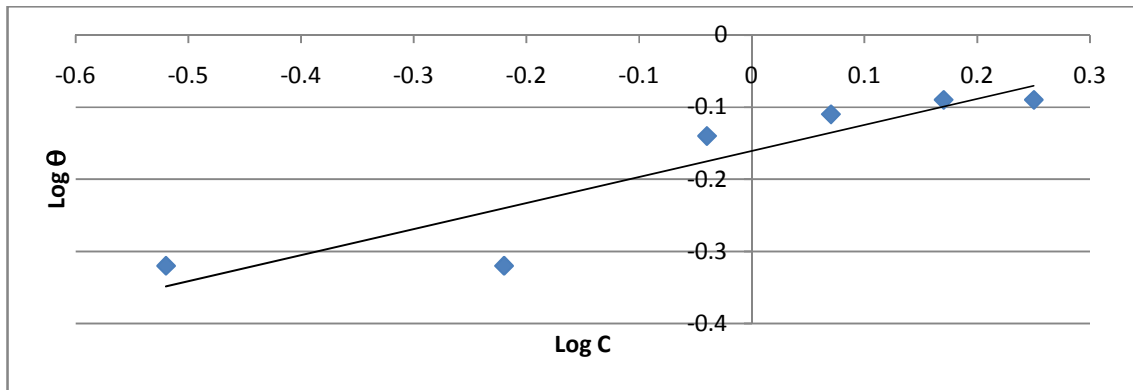**Figure 6. Tempkin adsorption isotherm for the inhibition of corrosion of mild steel by MTHL in ground water**

_____
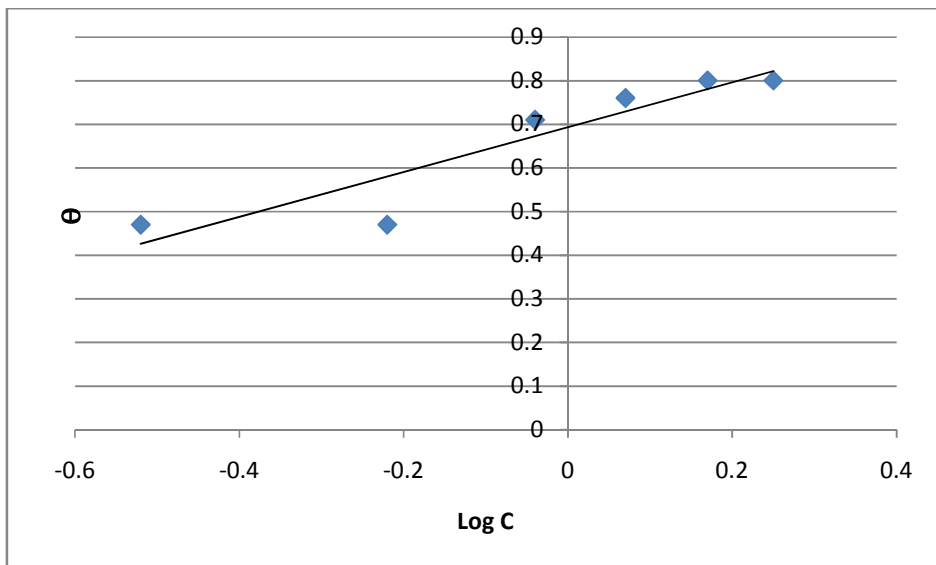
**Figure 7.  Freundlich adsorption isotherm for the inhibition  of corrosion of mild steel by MTHL in ground water**
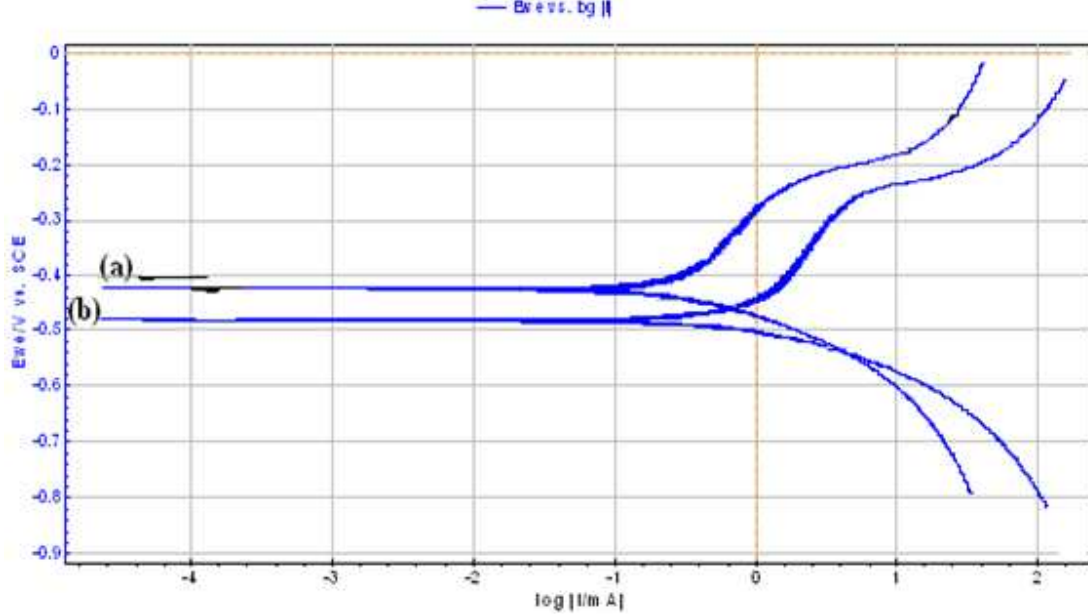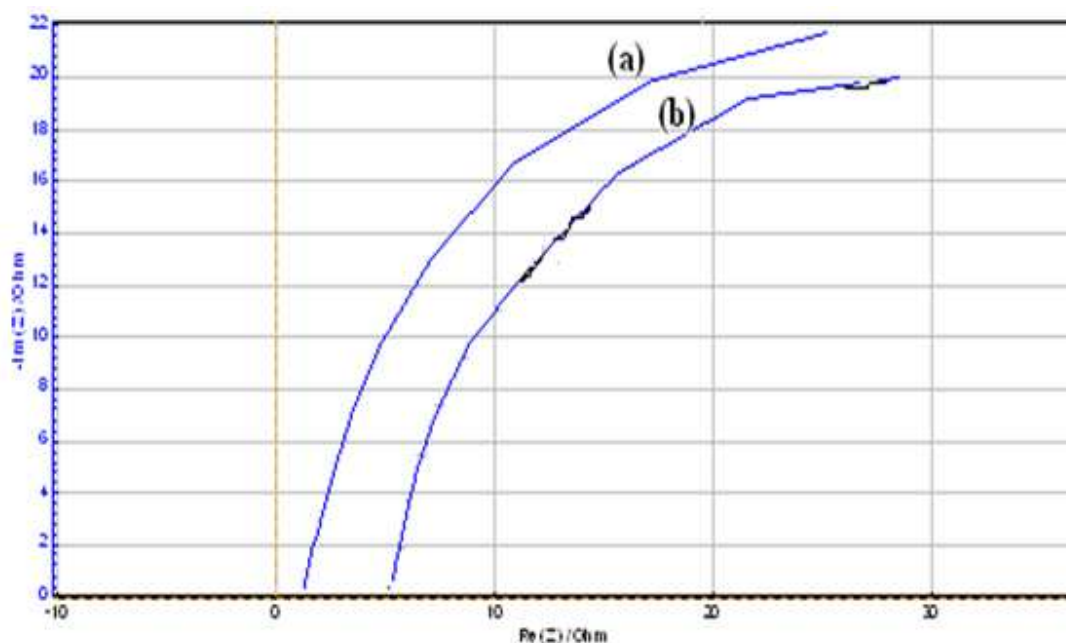


.

**Figure 8. Typical potentiostatic curve**



*(a) Tafel plot T*
*(a) Tafel plot for mild steel in ground water with MTHL*
*(b) Tafel plot for mild steel in ground water*

_____

**Figure 9. AC impedance of mild steel in various environments**



*(a) Nyquist diagram for mild steel in ground water*
*(b) Nyquist diagram for mild steel in ground water with MTHL extract*

**CONCLUSION**

The following conclusions were made from the following studies,

1. The corrosion rate of mild steel in ground water decreases with increase in concentration of MTHL.
2. The inhibition efficiency increases with respect to the concentration of the inhibitor and decreases with rise in temperature from 303K to 333K.
3. The maximum inhibition efficiency of MTHL is found to be 81.0% at 1.8(%v/v) of inhibitor from mass loss studies at 303K.
4. The decrease in the energy of activation values indicates that the addition of plant extract Metal dissolution and also indicates that decrease in the adsorption of the inhibitor on mild steel surface with increase in temperature.
5. The negative values of ΔG indicates that the MTHL is chemically adsorbed and spontaneous adsorption of inhibitors on the surface of mild steel.
6. The higher value of heat of adsorption also showed that the inhibition efficiency decrease With rise in temperature.
7. The low positive enthalpy value of adsorption is evident that the MTHL was strongly adsorbed on the mild steel was probably physisorption.
8. The adsorption of MTHL on mild steel surface from the acid solution followed Tempkin,Langmuir and Freundlich adsorption isotherms.
9. The results of polarization study showed that the formulation function as a mixed type inhibitor , more predominantly controls the anodic reactions.
10. The AC impedance spectral studies revealed the formation of a film with higher resistance than that of the blank solution.

_____

## REFERENCES

[1]Arora P, Kumar S, Sharma M K and   Mathur S P, *E J Chem.*,  **2007,4**(4), 450-456

[2] Al-Sehaibani H, *Materialwissenschaft   and Werkstofftechnik*, **2000,31**(2), 1060-1063

[3] Chaieb E, Bouyanzer A, Hammouti B and  Benkaddour M, *Appl Surf Sci.*, , **2005**, **246,** 199-206

[4]  Chaieb E, Bouyanzer A, Hammouti B,  Benkaddour M and Berrabah M, *Transactionsof   the   SAEST*, **2004**, **39,** 58-60

[5]  Chauhan L.R and Gunasekaran G,  *Corrosion Science*,  **2007**, **49**(3),1143-1161

[6] El-Etre A Y, Abdallah M, El-Tantawy Z  E, *Corrosion Science*,  **2005**, **47,** 385-395

[7] Olusegun K. Abiola N C, Oforka E E, Ebenso, *J Corrosion Sci Eng.*, , **2004**,  **5,** 10

[8] Orubite O K and Oforka N C, *Mater Lett.*,   **2004**, **58**(11),1768-1772

[9] Rehan H H, *Materialwissenschaft and   Werkstofftechnik.*,  **2003**, **34**(2), 232-237

[10] Saratha R and Priya S V,  National    Seminar   on  Current Developments in chemistry(NSCDC-  07), Organized by  Department of chemistry,Bharathiar   University, Coimbatore, 18th & 19th   Jan **2007**.

[11] Saratha R and Priya S V, Inhibition of  mild steel corrosion in 0.5 M H2SO4 by   an eco- friendly inhibitor, National   Seminar on Recent Trends in Chemistry, Organized by Department of    Chemistry, Nirmala College for women,  Coimbatore, 1$^{st}$ & 2$^{nd}$ March  **2007**.

[12] Saratha R, Kasthuri S, Sivakamasundari   S, *J Electrochem Soc India,* **2003**,  **52**(4),  163-168

[13] Saratha R, Savitha R, and   Sivakamasundari S, *J Electrochem So India,* , **2003***,* **52**(2),  59-63

[14]Sheyreese M, Vincent and Cyril B Okhio, *J Corrosion Sci Eng.*, , , **2005**, **7,** 36

[15] Smita A. Verma and Mehta G.N, *Bull   Electrochem.*,  **1999**, **15**(2), 67-70

[16] Tripti Jain, Rittu Chowdhary, Paresh   Arora and Mathur S P, *Bull lectrochem.*, **2005**,   **21**(1), 23-27

[17] K. Lakshmi Prabha, Shameela Rajam, B. R.Venkatraman, *Der Chemica Sinica*, **2012**, 3(1): 114-123

[18] Baban K. Magarea and Milind B. Ubaleb. Der Chemica Sinica, **2011**, 2 (2):158-164.

[19] Yadav. M.  Debasis Behera and Usha Sharma.  Der Chemica Sinica, **2012**, 3(1):262-268.

[20] Schmitt G, *Br Corros J.*,  **1984**, **19**(4), 165

[21] C.S.S.R. Kumar, M. Srinivas, S.  Yakkundi, *Phytochem. ,* **1996,**43 ,451

[22] O. Schaaf, A. P. Jarvis, S. A. van der  Esch, G. Giagnacovo, N. J. Oldham, *J.Chromatogr.* **2000**, 886 ,89

[23] V.U. Khuzhaeu, S. F. Aripova, *Chem.  Nat. Comp.*,**2000**,36 ,41

[24] P.C. Okafor, E. E. Ebenso, *Pigment   Resin. Tech.*, **2000**, 36 ,134 22.  P.C. Okafor,  M.E.Ikpi,  I.E. Uwah, E.E. Ebenso, U.J. Ekpe, S.A. Umoren,  *Corros. Sci,* **2008**,  50 ,2310

[25] A.U. Ogan, *Phytochem. Rep.* **1971**, 99, 441

[26] E.E. Ebenso, U. J. Ekpe, *W. Afr. J. Bio.  Appl. Chem.,***1996***,*  41, 21

[27] M. Kliskic, J. Radosevic, S. Gudic, V.  Katalinic, *J. Appl. Electrochem.* 30 ,  823(**2000**)

[28]E.E. Ebenso, U. J. Ibok, U. J. Ekpe, S. Umoren, E. Jackson, O. K. Abiola, N. C. Oforka,   S. Martinez, *Trans. Of SAEST,***2004**,  39 ,117 .

[29] G. Gunasekaran, L.R. Chauhan, *Electrochim. Acta,,* **2004**, 49 ,4387

[30] P.C. Okafor, U. J.  Ekpe, E. E. Ebenso, E.  M. Umoren, K. E. Leizou, *Bull.  Electrochem.* **2005**,  21,347

[31] A.Y. El-Etre, M. Abdallah, Z.E. El- Tantawy, *Corros. Sci. ,***2005**, 47,385

[32] E.E. Oguzie, *Mater. Chem. Phys,* **2006**, 99,  441

[33] E.E. Oguzie, A. I. Onuchukwu, P. C. Okafor, E. E., Ebenso, *Pigment Resin Tech.* , **2006**, 35, 63

[34] A.M. Abdel-Gaber, B.A. Abd-El-Nabey,   I.M. Sidahmed, A.M. El-Zayady,  M. Saadawy,  *Corros.Sci. ,***2006**, 48 ,2765

[35] S.A. Umoren, I. B. Obot, E. E. Ebenso,  P. C. Okafor, O. Ogbobe, E. E. Oguzie,   *Anti-Corros. Meth. Mater*. 53 , 277(**2006**)

[36] P.C. Okafor, U. J. Ekpe, E. E. Ebenso, E.  Oguzie, N. S. Umo, A. R. Etor, *Trans. SAEST,* **2006**,   41,82

[37] P.B. Raja, M.G. Sethuraman, *Mater.  Letts.* **2008**, 62 ,113