Temperature studies of *Thespesia populnea* fruit extract as green corrosion inhibitor for mild steel in 1N H2SO4 solution

Aparna C[1], Indulekha M S[2], W.Anushya Prama Kumari[3], T Epsiba[4]

[1,3,4]Assistant professor, Department of chemistry Dhanalakshmi Srinivasan College of Engineering (Autonomous), Coimbatore Tamilnadu, India

[2]P-G student, Nirmala College for Women Coimbatore Tamil nadu India

Abstract: Thespesia populnea. ex-Correa (Malvaceae) is commonly known as "Indian tulip tree".

The plant has been used as an astringent, antibacterial, anti-inflammatory, antinociceptive and hepatoprotective in Indian system of traditional medicine.In this study Thespesia populnea fruit extract (TPF) was used as corrosion inhibitor for mild steel in 1N H_2SO_4 medium. From temperature studies it was found that the corrosion rate decreased with increase in concentration of the inhibitor. Also, temperature studies showed that the inhibition efficiency was found to increase with the increase in concentration of the inhibitor. At high temperature the extract under study has higher inhibition efficiency.

Key words: Corrosion, Inhibition efficiency, Corrosion rate, Mild steel, green inhibitor, Thermal analysis.

1. INTRODUCTION

Corrosion is a natural process where metals and alloys try to attain their more stable form [1] due to chemical attack or by reaction with its environment [2]. Also, corrosion can be initiated by natural or manmade activities [3]. In general, metals corrosion can be defined as the deterioration of desired metals properties on interaction with certain elements that are present in the environment which is a normal and unavoidable process [4]. Corrosion is known to be harmful to the environment and also to human well-being. The causes of corrosion in metals and alloys vary. The causes include the presence of water as moist in the air, bases or acidic medium, salts, liquid chemicals, aggressive metal polishes as well as hazardous gases that can initiate corrosion on the metal surface [5]. Corrosion is also influenced by surrounding temperatures [3]. In addition, the presence of certain bacteria species over steel can accelerate an already established corrosion process [6] and promote the conditions to its development [7]. The high cost associated with corrosion, due to the replacement of rusted metals, can be reduced by using corrosion inhibitors [8]. The use of common corrosion inhibitors is sometimes limited, since these are based on dangerous substances for human health, such as chromium- based treatments [9]. The temperature study gives the effect of corrosion rate on mild steel in acidic environment [10].

2. MATERIALS AND METHODS

2.1 PREPARATION OF *THESPESIA POPULNEA* FRUIT EXTRACT (TPF)

The fruits of *Thespesia populnea* were collected from the garden, dried in shade and powdered using mechanical blender. About 75g of the powdered sample is weighed and mixed with 1N H_2SO_4 solution in a round bottom flask and boiled for 3 hrs. To avoid bumping porcelain bits are added. The boiled solution is kept overnight and the settled residue is filtered. The filtrate is kept in an air tight container.

2.2 SPECIMEN PREPARATION

Rectangular mild steel (MS) specimens of dimension 1cm×4cm×0.2cm were taken and mechanically polished using emery paper of grade 120.

2.3 TEMPERATURE STUDY

Previously weighed mild steel specimens are suspended in 100ml test solution, by using glass hooks with and without different concentrations of TPF extract for 1hr in the temperature range 303K-333K in a thermostat ("Technico" serological digital pit water bath). Then the specimens are washed and dried well. The weight of the specimen before and after immersion is measured.

The corrosion rates (CR) were calculated by usig the following formula;

$$CR = \frac{534*W}{D*A*t}$$

- W-Weight loss
- D-Density of metal
- A-Area of the metal
- t-time period in hours

The corrosion inhibition efficiency (IE) was calculated using the following equation;

$$IE(\%) = \frac{CRBlank - CRInhibitor}{CRBlank} *100$$

- Blank- Weight loss in the absence of inhibitor.
- Inhibitor- Weight loss in the presence of inhibitor

3. RESULT AND DISCUSSION

3.1 TEMPERATURE STUDY

Table. 1 Corrosion rate of mild steel and inhibition efficiency of TPF extract at different temperatures

Concentration of TPF extract (v/v)	303K		313K		323K		333K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	1696	-	2215	-	7950	-	17226	-
0.01	1199	29	1461	34	2067	74	13091	24
0.05	1024	39	1264	42	1461	81	12590	26
0.1	741	56	863	61	1225	84	9096	47
0.5	479	71	754	65	1071	86	1347	92
1	457	73	566	74	985	87	1046	93
1.5	392	76	405	81	584	92	862	94
2	348	79	370	83	549	93	771	95
2.5	174	89	252	88	536	93	730	95
3	65	96	170	92	222	97	523	96

The result obtained from the temperature study is represented in Table.1. After immersing mild steel in fruit extract the CR was found to decrease with increase in concentration of the inhibitor at various temperature. At 303K the corrosion rate decreased from 1696 mpy to 65 mpy, at 313K the corrosion rate decreased from 2215 mpy to 170 mpy, at 323K the corrosion rate decreased from 7590 mpy to 222 mpy, at 333K the corrosion rate decreased from 17226 mpy to 523 mpy, Similarly, the inhibition efficiency of 29% to 96% is obtained at 303K, at 313K the inhibition efficiency become from 34% to 94%, at 323K the inhibition efficiency gradually increases from 74% to 97%, at the inhibition efficiency becomes 24% to 96%.

3.2 ADSORPTION STUDIES

Corrosion inhibition is a surface phenomenon. The interaction of the inhibitor with the surface can be estimated from the experimental data. The inhibition efficiency depends on different factors such as the type, number of active sites at the metal surface, charge density, molecular size of the inhibitor, metal inhibitor interactions and the metallic complex formation. Adsorption isotherms give information about metal inhibitor interaction. Adsorption isotherms are very useful in determining the mechanism of the inhibition reaction. Most frequently used adsorption isotherms are Langmuir, Temkin, Freundlich, Arrhenius and El-awady isotherms. The experimental data obtained with different inhibitor concentration of the TPF extract in the H_2SO_4 medium at different temperatures from 303K to 333K were applied to different adsorption isotherm equations. Degree of surface coverage θ was calculated based on inhibition efficiency which in turn calculated from weight loss measurement as

θ = (IE%/100)

Adsorption parameters for various adsorption isotherms for mild steel in 1N H_2SO_4 in the presence of TPF extract are calculated. It was found that the data were fit in the Langmuir, Temkin, Freundlich, Arrhenius and El-awady isotherms.

3.3 ISOTHERM CALCULATION

3.3.1 ARRHENIUS ISOTHERM

Arrhenius adsorption isotherm represents the variation in the amount of adsorbate adsorbed on the surface of the adsorbent at a given temperature.

Table 2: Arrhenius isotherm for different temperature of TPF extract

CONCENTRATION	303K	313K	323K	333K
	LogCR	LogCR	LogCR	LogCR
B	3.229	3.345	3.9	4.236
0.01	3.0788	3.164	3.315	4.1169
0.05	3.01	3.101	3.164	4.1
0.1	2.869	2.936	3.088	3.958
0.5	2.68	2.877	3.029	3.129
1	2.659	2.752	2.993	3.019
1.5	2.593	2.607	2.766	2.935
2	2.541	2.568	2.739	2.887
2.5	2.2405	2.401	2.729	2.863
3	1.8129	2.23	2.346	2.718

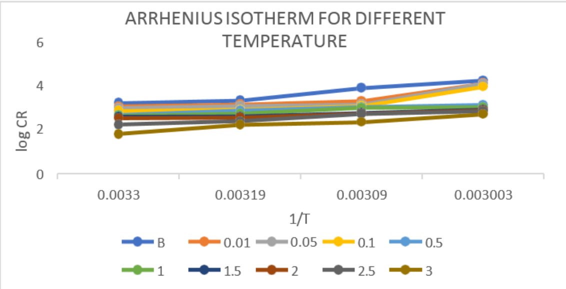

Fig 1: Arrhenius isotherm for different temperature of TPF extract

3.3.2 FREUNDLICH ISOTHERM

Freundlich adsorption isotherm gives the empirical relation between the quantity of adsorbate adsorbed by a unit mass of adsorbent on a given temperature.

Table 3: Freundlich isotherm for different temperature of TPF extract

LogC	303K	313K	323K	333K
	Logθ	Logθ	Logθ	Logθ
-2	-0.537	-0.468	-0.13	-0.619
-1.301	-0.408	-0.376	-0.091	-0.585
-1	-0.251	-0.214	-0.075	-0.327
-0.301	-0.148	-0.187	-0.065	-0.036
0	-0.136	-0.13	-0.06	-0.0315
0.176	-0.119	-0.091	-0.036	-0.026
0.301	-0.102	-0.08	-0.0315	-0.022
0.397	-0.05	-0.055	-0.0315	-0.022
0.477	-0.017	-0.036	-0.0132	-0.0177

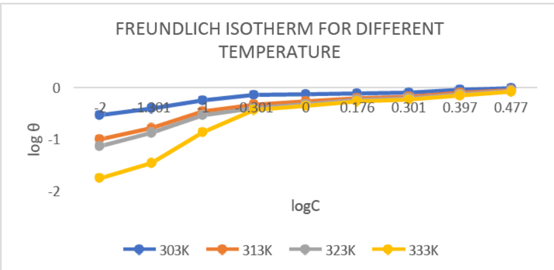

Fig 2: Freundlich isotherm for different temperature of TPF extract

3.3.3 TEMKIN ISOTHERM

Temkin adsorption isotherm shows that the adsorption heat of all molecules decreases linearly with increase in the surface coverage of the adsorbent.

Table 4: Temkin isotherm for different temperature of TPF extract

LogC	303K	313K	323K	333K
	θ	Θ	θ	Θ
-2	0.29	0.34	0.74	0.24
-1.01	0.39	0.42	0.81	0.26
-1	0.56	0.61	0.84	0.47
-0.301	0.71	0.65	0.86	0.92
0	0.73	0.74	0.87	0.93
0.176	0.76	0.81	0.92	0.94

0.301	0.79	0.83	0.93	0.95
0.397	0.89	0.88	0.93	0.95
0.477	0.96	0.92	0.97	0.96

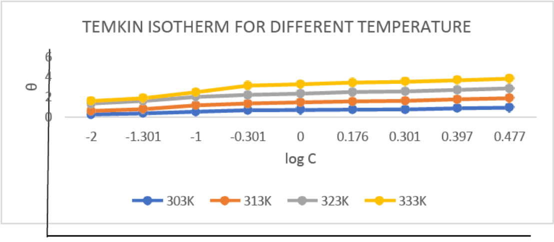

Fig 3: Temkin isotherm for different temperature of TPF extract

3.3.4 EL-AWADY ISOTHERM

El-awady isotherm gives the details of active sites occupied by the adsorbate on the adsorbent surface.

Table 5: El-awady isotherm for different temperature of TPF extract

LogC	303K	313K	323K	333K
	Logθ /1-θ	Logθ /1-θ	Logθ /1-θ	Logθ /1-θ
-2	-0.757	-0.709	-0.502	-0.815
-1.301	-0.67	-0.649	-0.481	-0.79
-1	-0.572	-0.55	-0.473	-0.618
-0.301	-0.512	-0.534	-0.467	-0.452
0	-0.506	-0.502	-0.465	-0.45
0.176	-0.496	-0.481	-0.452	-0.447
0.301	-0.487	-0.476	-0.45	-0.445
0.397	-0.46	-0.462	-0.45	-0.445
0.477	-0.443	-0.452	-0.44	-0.443

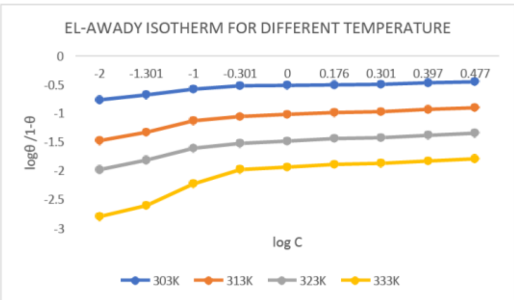

Fig 4: El-awady isotherm for different temperature of TPF extract

3.3.5 LANGMUIR ISOTHERM

Langmuir adsorption isotherm defines the linear adsorption at higher solute metal concentration with a maximum surface coverage.

Table 6: Langmuir isotherm for different temperature of TPF extract

CONCENTRATION	303K	313K	323K	333K
	C/ θ	C/ θ	C/ θ	C/ θ
B				
0.01	0.0344	0.0294	0.0135	0.0416
0.05	0.1282	0.119	0.0617	0.1923
0.1	0.1785	0.1639	0.119	0.2127
0.5	0.7042	0.7692	0.5813	0.5434
1	1.3698	1.3513	1.1494	1.0752
1.5	1.9736	1.8518	1.6304	1.5957
2	2.5316	2.4096	2.1505	2.1052
2.5	2.8089	2.8409	2.6881	2.6315
3	3.125	3.2608	3.0927	3.125

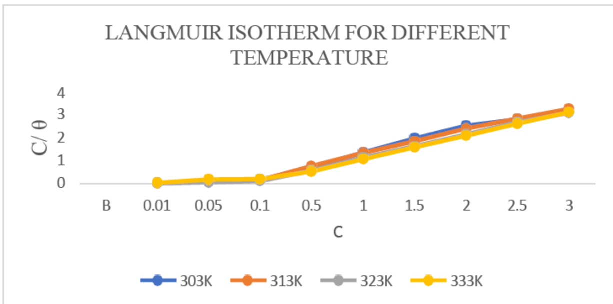

Fig 5: Langmuir isotherm for different temperature of TPF extract

3.4 THERMODYNAMIC PARAMETERS

Thermodynamic parameters for adsorption of the TPF extract on mild steel in 1N H2SO4

Table 7: Values of Gibb's free energy at different temperature of TPF extract

	303 K	313 K	323 K	333 K

C	ΔG	ΔG	ΔG	ΔG
0.01	17.71603	17.93282	17.54517	18.79362
0.05	14.02488	14.08454	12.92748	15.00736
0.1	12.36688	12.27843	10.83967	15.59361
0.5	7.859321	8.110675	6.50738	17.99492
1	6.002817	5.942008	4.603337	16.61216
1.5	4.785918	4.357842	2.499243	16.00589
2	3.822176	3.414213	1.465195	15.76709
2.5	1.931013	2.121777	0.902964	15.20486
3	-0.88642	0.752793	-1.58516	15.3341

Thermodynamic parameters for the adsorption of TPF extract in 1N H_2SO_4 is shown in table 7. The value of ΔG calculated are in the range -1.58 KJ/mol to 18.79KJ/mol. This indicates that the plant constituents are adsorbed on the metal surface by strong physical adsorption process. Physical adsorption is a multilayer adsorption in which the first layer is adsorbed on the adsorbent and the other layers condense on the first layer. In physical adsorption molecules are attached to the surface through weak bonds such as Vander Waals forces, hydrogen bonding or hydrophobic interactions.

4. CONCLUSION

- The green inhibitor *Thespesia populnea* fruit extract is an efficient for mild steel corrosion in 1N H_2SO_4 medium.
- The temperature study exhibited that, the inhibitor is efficient at high temperature as well, maximum efficiency of 97% was obtained at 323K at the concentration 3.0 (%v/v) of TPF extract.
- The thermodynamic parameter revealed that the inhibitor is adsorbed on the metal surface by strong physical adsorption, the molecules are attached to the surface through weak bonds such as Vander Waals forces, hydrogen bonding or hydrophobic interactions.

5. REFERANCE

[1] O. S. Shehata, L. A. Korshed, and A. Attia, “Green Corrosion Inhibitors, Past, Present, and Future,” Corros. Inhib. Princ. Recent Appl., 2018, doi: 10.5772/intechopen.72753.

[2] P. Rathi, “Plant Extracts As Green Corrosion Inhibitors in Various Corrosive Media- a Review,” World J. Pharm. Pharm. Sci., pp. 482–514, 2017, doi: 10.20959/wjpps20174-8903.

[3] M. Goyal, S. Kumar, I. Bahadur, C. Verma, and E. E. Ebenso, “Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review,” J. Mol. Liq., vol. 256, pp. 565–573, Apr. 2018, doi: 10.1016/J.MOLLIQ.2018.02.045.

[4] S. A. Umoren, M. M. Solomon, I. B. Obot, and R. K. Suleiman, “A critical review on the recent studies on plant biomaterials as corrosion inhibitors for industrial metals,” J. Ind. Eng. Chem., vol. 76, pp. 91–115, Aug. 2019, doi: 10.1016/J.JIEC.2019.03.057.

[5] P. B. Raja et al., “Reviews on Corrosion Inhibitors: A Short View,” https://doi.org/10.1080/00986445.2016.1172485, vol. 203, no. 9, pp. 1145–1156, Sep. 2016, doi: 10.1080/00986445.2016.1172485.

[6] Lin, J, Ballim, and R, “Biocorrosion control: Current strategies and promising alternatives,” African J. Biotechnol., vol. 11, no. 91, pp. 15736– 15747, Nov. 2012, doi: 10.5897/AJB12.2479.

[7] C. Rubio, C. Ott, C. Amiel, I. Dupont-Moral, J. Travert, and L. Mariey, “Sulfato/thiosulfato reducing bacteria characterization by FT-IR spectroscopy: a new approach to biocorrosion control,” J. Microbiol. Methods, vol. 64, no. 3, pp. 287–296, Mar. 2006, doi: 10.1016/J.MIMET.2005.05.013.

[8] M. Ladan, W. J. Basirun, S. N. Kazi, and F. A. Rahman, “Corrosion protection of AISI 1018 steel using Co-doped TiO2/polypyrrole nanocomposites in 3.5% NaCl solution,” Mater. Chem. Phys., vol. 192

[9] S. Jiang, F. Chai, H. Su, and C. Yang, “Influence of chromium on the flow-accelerated corrosion behavior of low alloy steels in 3.5% NaCl solution,” Corros. Sci., vol. 123, pp. 217–227, Jul. 2017, doi: 10.1016/J.CORSCI.2017.04.024.

[10] D. S. Zinad, Q. A. Jawad, M. A. M. Hussain, A. Mahal, L. Mohamed, and A. A. Al-Amiery, “Adsorption, temperature and corrosion inhibition studies of a coumarin derivatives corrosion inhibitor for mild steel in acidic medium: Gravimetric and theoretical investigations,” Int. J. Corros. Scale Inhib., vol. 9, no. 1, pp. 134–151, 2020, doi: 10.17675/2305-6894-2020-9-1-8.