



# Extract Of The Ficus Benghalensis And Trigonella Foenum Graecum Leaves As A Sustainable Corrosion Inhibitor For Mild Steel In Hydrochloric Acid.

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## Abstract

In this study, the impact of extracts from *Ficus benghalensis* and *Trigonella foenum graecum* leaves on corrosion inhibition are investigated at  $28 \pm 1$  °C in the open air. In 1 N hydrochloric acid solution, weight loss, Langmuir isotherm adsorption, and thermodynamic parameters like activation energy ( $E_a$ ), free energy of adsorption ( $\Delta G^0_{ads}$ ), and enthalpy of adsorption ( $\Delta H^0_{ads}$ ) were employed to evaluate these leaf extracts as an affordable, environmentally friendly, and effective corrosion inhibitor for mild steel. The Langmuir isotherm demonstrates that adsorption, including physical adsorption, is the preferred method of depositing an organic inhibitor. The rise in IE% with concentration and the activation parameters, which indicated considerable chemisorption of both plant extracts on mild steel surface, were used to explain the inhibitory mechanism of the leaf extracts of both plants. The potential application of *T. foenum graecum* and *F. benghalensis* extract as a mild steel corrosion inhibitor in an acidic medium is confirmed by the close concurrence between the results obtained using different techniques.

Keyword: corrosion inhibition, weight loss, Langmuir isotherm adsorption.

## Introduction

Inhibiting metal corrosion is one of the industry's most significant problems. Reducing the rate at which various components of oil production facilities, tubing, and pipelines from the wellhead equipment corrode extensively is the primary issue. When dissolved carbon dioxide, hydrogen sulphide, and salts come into contact with a metal surface, corrosion occurs (Alimohammadi *et al.*, 2023; Bardal, 2004).

In various media, a variety of inorganic compounds, including organic complexes of manganese and chromium, were utilised as corrosion inhibitors (Tabesh *et al.*, 2019; Verma *et al.*, 2018; Verma *et al.*, 2017). These inexpensive compounds effectively reduced the corrosion of many metals, including Fe, Al, and Cu (Singh *et al.*, 2016). But using them as corrosion inhibitors pollutes the environment. As a result, they are less relevant (El-Tabesh *et al.*, 2020).

Green corrosion inhibitors, or environmentally friendly corrosion inhibitors, are gaining popularity these days. These naturally occurring inhibitors have various benefits. They are renewable, easily obtainable, biodegradable, efficient, and kind to the environment (Dakhil *et al.*, 2018; Raghavendra, 2019). It is simple to extract those environmentally beneficial inhibitors from plants. Separating, identifying, and correlating various species with the efficiency of inhibition is a crucial next step. Furthermore, an investigation into the potential for synergism or antagonistic relationships that guarantee an ideal degree of inhibition was conducted by examining the inhibitory effects of the extracted species either alone or in combination (Seo *et al.*, 2015).

The extracts with functional groups for oxygen, sulphur, and nitrogen demonstrate excellent inhibition. Due to the fact that these groups' free electrons can attach to metal ions that have partially dissolved, delaying further corrosion and dissolution (Aribo *et al.*, 2015).

Ecofriendly corrosion inhibitors have been the subject of recent research. Weight loss, electrochemical polarisation, and impedance measurement techniques were used to assess the effectiveness of *Ficus benghalensis* (FB) bark acid extract on the corrosion inhibition of MS in 2N, 3N, and 4N hydrochloric acid at different temperatures. It was shown that when the inhibitor's concentration increased, so did its effectiveness (Subhashini *et al.*, 2018). In the process of making phosphate fertiliser, fenugreek seed extract (Fen) and Cape gooseberry leaf extract (CgL) work as environmentally friendly corrosion inhibitors for mild steel. As the concentration of the extract increases, the inhibition effectiveness rises and eventually reaches around 80%. The creation of a smooth layer on steel in the presence and absence of Fen and CgL extracts is made clear by a SEM micrograph, which may be the result of the extracts' chemical contents adsorbing (Abdel-Gaber *et al.*, 2022).

*Phyllanthus amarus* leaf extract was used to study the suppression of carbon steel corrosion (Anupama *et al.*, 2016). Plant extract was adsorbed according to the Langmuir isotherm. Using electrochemical techniques, energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM), an alkaloids extract of *Geissospermum* leaves was investigated as an inhibitor for carbon C-steel corrosion (Faustin *et al.*, 2015).

Additionally, extracts from *Acalypha torta* leaves were utilised to stop mild steel from corroding. The inhibitory efficiency was measured using UV-visible spectroscopy, weight loss, and an electrochemical process. At 1000 ppm extract solution, the reported inhibitory efficacy was around 90% (Krishnegowda *et al.*, 2013). In order to investigate the inhibitory impact of the Aloe Vera leaf extract in a 1 M H<sub>2</sub>SO<sub>4</sub> solution on corrosion, electrochemical and SEM methods were utilised. According to Mehdipour *et al.* (2015), the findings showed that plant extract has a 98% IE% at 30% v/v concentration and functions as a mixed type inhibitor for mild steel. *Citrus aurantium* leaf extracts have been used in aqueous acid medium as a mild steel corrosion inhibitor that is environmentally benign. The outcomes showed that molecular extract adsorption happened in accordance with Langmuir isotherm (Hassan *et al.*, 2013).

The Indian National Tree, *Ficus benghalensis*, is a symbol of spiritual wisdom and everlasting life. To address a range of ailments, including antioxidants, antidiabetic, anti-inflammatory, anticancer, antitumor and antiproliferative, antimutagenic, antimicrobial, anti-helminthic, hepatoprotective, wound healing, anticoagulant, immunomodulatory activities, antistress, and toxicity, root and stem bark is commonly prepared in decoction form (Patel and Gautam, 2014; Joseph and Raj, 2010). Flavonoids, phenols, terpenoids, terpenes quinone, and furanocoumarin derivatives, such as rhein, psoralen, and bergapten, are abundant in the leaves and bark of *F. Benghalensis* (Rao *et al.*, 2014; Naquvi *et al.*, 2015).

Several active ingredients found in fenugreek seeds have been identified and isolated. These include polyphenolic flavonoids, which have been shown to exhibit the most common properties, including hypoglycemic, hypocholesterolemic, hypotriglyceridemic, and antiperoxidative properties; steroid saponins, which have been shown to exhibit anti-inflammatory, uterine, and lactation-stimulating properties; polysaccharides, like galactomannans, have been shown to have antidiabetic effects; and an amino acid, 4-hydroxyiso-leucine, has been demonstrated to have insulin-mimetic properties (Broca *et al.*, 2004; Yadav and Baquer, 2014).

## Materials

### Extraction of plants Leaves

In the current investigation, weight loss and electrochemical techniques were used to explore the potential corrosion inhibitory effects of the leaf extracts of *T. foenum graecum* and *F. benghalensis*. The leaves of both plants were gathered at Ajmer, Rajasthan. The gathered leaves were sun-dried, crushed into a powder, and then steeped in 95% ethanol for three days. The Soxhlet technique was then used to create the extract. Ethanol, methanol, and water may all be easily dissolved in the produced dry plant extract.

To assess weight loss, mild steel specimens measuring 2.5 cm X 1 cm X 0.1 cm were employed.

### Weight Loss Method

Weight loss is the method most frequently employed to calculate corrosion damage. You can estimate how much metal the item would lose due to corrosion by weighing it both before and after exposure (Ikpesu, 2014).

This was used to calculate the inhibitor's effectiveness in preventing inhibition using the formula:

$$IE\% = \frac{w_0 - w_i}{w_0} \times 100$$

IE- Inhibition efficiency; W is the weight loss with (i) or without (0) influence of the inhibitor.

Surface coverage ( $\theta$ ) was calculated using the formula

$$\text{Surface Coverage } (\theta) = \frac{\Delta M_u - \Delta M_i}{\Delta M_u}$$

### Langmuir Adsorption Isotherm

To determine which adsorption isotherm best described the adsorption of leaf extracts on the mild steel surface in HCl solution, a number of adsorption isotherms, including Langmuir, Frumkin, Temkin, and Freundlich, were employed. The experimental results were best fitted to the Langmuir adsorption isotherm, can express as-

$$C/\theta = (1/K_{ads}) + C$$

Where C is a concentration of inhibitor molecules,  $\theta$  is surface coverage, and  $K_{ads}$  is the equilibrium constant of the adsorption process.

### Determination of Thermodynamic parameters:

Various thermodynamic parameters such as activation energy ( $E_a$ ), free energy of adsorption ( $\Delta G^0_{ads}$ ), and enthalpy of adsorption ( $\Delta H^0_{ads}$ ) were calculated from the results of temperature study.

### Results and Discussion

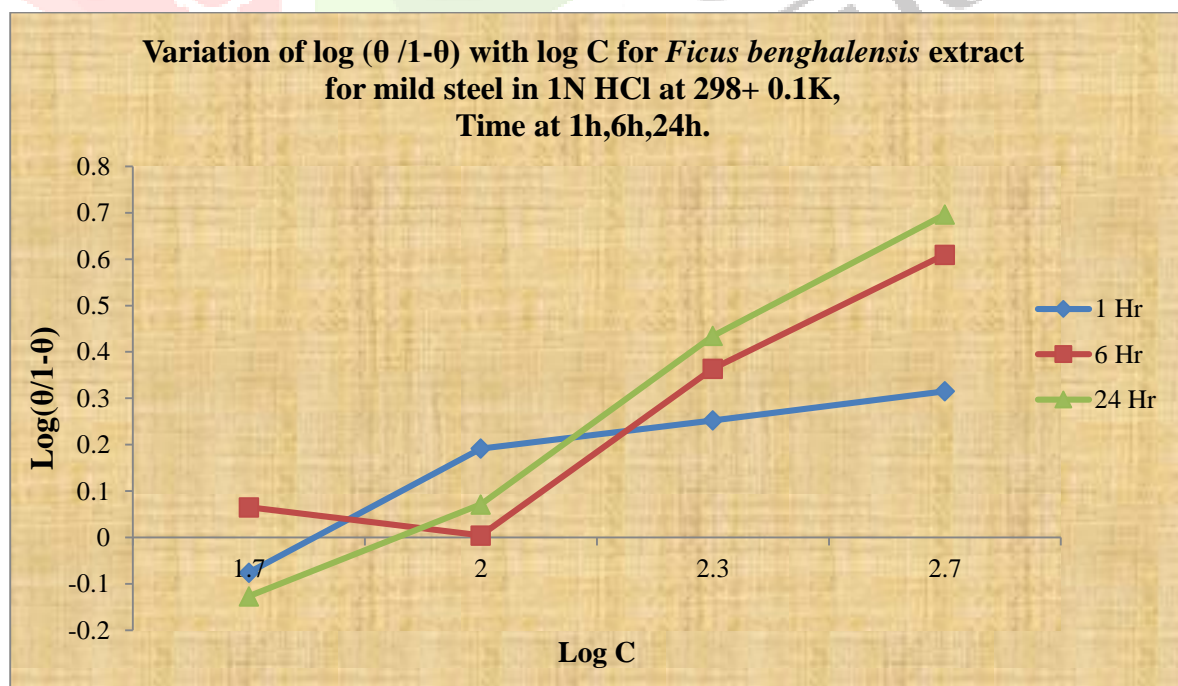
The effect of different concentrations (i.e., 50, 100, 200 and 500 ppm) of the extracts (ethanol fraction) obtained from two plants was studied after immersion in 1 N HCl solution in open air at  $28 \pm 1$  °C and the estimated average corrosion rate.

The corrosion parameters such as surface coverage ( $\theta$ ), the percentage of inhibition efficiency (IE %) and corrosion rates (mmpy) are presented in Table 1 for *F. benghalensis* leaves extract and Table 2 for *T. foenum graecum* leaves extract and the variation of corrosion inhibition efficiency with inhibitor concentration is also represented in Figures 1 for *F. benghalensis* leaves extract and 2 for *T. foenum graecum* leaves extract. Figures show the weight loss–time curves for mild steel in 1 N HCl without and with different concentrations of leaves extracts at different time (1hr, 6hrs and 24 hrs) at 298K temperature. Plots demonstrate a considerable reduction in material loss ( $\text{g cm}^{-2}$ ) when extracts are present relative to a blank acid solution. Furthermore, the quantity of material loss was shown to be concentration-dependent. a tendency of declining

inhibitory effectiveness for all systems under study as time increased. This implies that a portion of the adsorbed inhibitor may have desorption from the metal surface.

**Table:1** Mass Loss measurement ( $\Delta M$ ), Corrosion Rate (mmpy), Inhibition Efficiency (IE %), Surface Coverage ( $\theta$ ) of *F. benghalensis* leaves extract inhibitors for mild steel in 1.0 N HCl at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm<sup>2</sup>

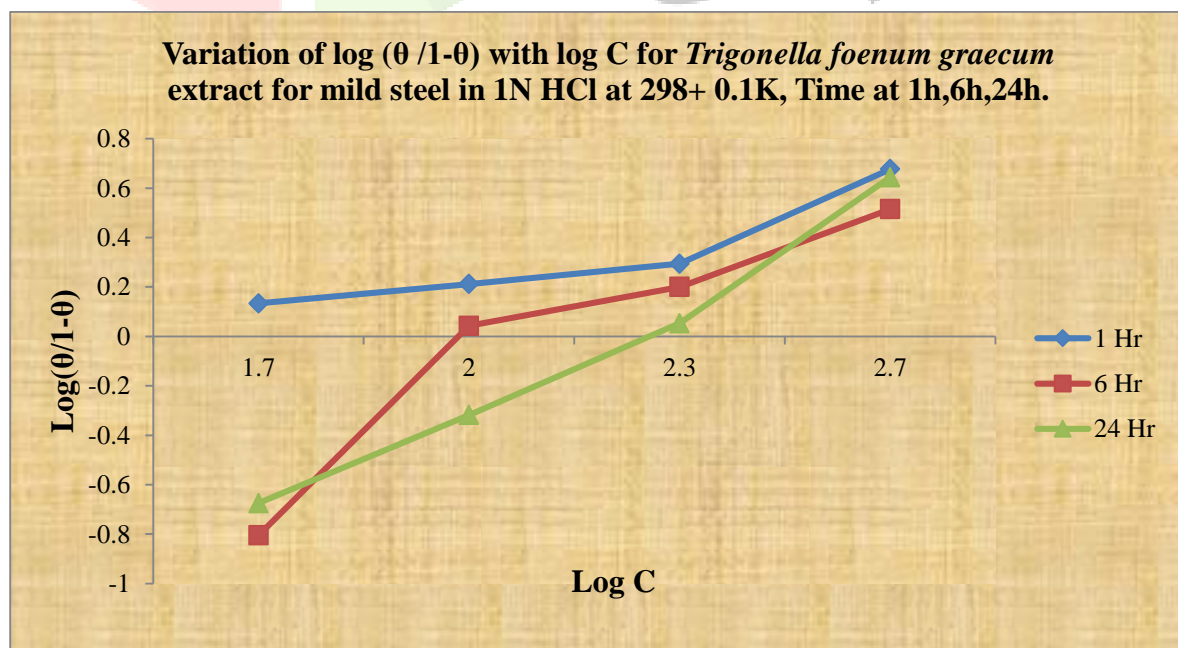
S. N O .	Inhibitor Conc.	Mass Loss( $\Delta M$ ) mg			Inhibition Efficacy (IE %)			Corrosion Rate (mmpy)			Surface Coverage( $\theta$ )			log( $\theta/1-\theta$ )			Log c
		1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	
1	Blank	93	338	473	-1.09	-48.25	17.45	22.318	235.832	330.026	-0.0108	-0.4824	0.174				
2	50	50	265	328	45.65	53.75	42.76	11.999	184.898	228.855	0.45652	0.53752	0.427	-0.075	0.0653	-0.126	1.698
3	100	36	285	263	60.87	50.26	54.10	8.639	198.853	183.503	0.60869	0.50261	0.541	0.1918	0.0045	0.0714	2
4	200	33	173	154	64.13	69.81	73.12	7.919	120.707	107.450	0.64130	0.6980	0.731	0.2523	0.3640	0.4346	2.301
5	500	30	113	96	67.39	80.28	83.25	7.199	78.843	66.982	0.67391	0.80279	0.832	0.315	0.6096	0.6962	2.698



**Figure:1**-Variation of log ( $\theta / 1-\theta$ ) with log C for *F. benghalensis* leaves extract inhibitors for mild steel in 1.0 N HCl at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm<sup>2</sup>

**Table: 2** Mass Loss measurement ( $\Delta M$ ), Corrosion Rate (mmpy), Inhibition Efficiency (IE %), Surface Coverage ( $\theta$ ) of *T. foenum graecum* leaves extract inhibitors for mild steel in 1.0 N HCl at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm<sup>2</sup>

S. No.	Inhibitor Conc.	Mass Loss( $\Delta M$ ) mg			Inhibition Efficacy (IE %)			Corrosion Rate (mmpy)			Surface Coverage( $\theta$ )			log( $\theta/1-\theta$ )			Log c
		1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	
1	Blank	93	406	512	1.09	0	10.645	22.318	283.2784	357.2378	0.01087		0.1064				
2	50	39	351	473	57.61	13.5467	17.452	9.359	244.9032	330.0263	0.576087	0.1354	0.1745	0.1332	0.8049	0.6748	1.698
3	100	35	193	387	61.96	52.4630	32.460	8.399	134.6619	270.0215	0.619565	0.5246	0.3246	0.2118	0.04282	-0.318	2
4	200	31	157	269	66.30	61.3300	53.054	7.439	109.5436	187.6894	0.663043	0.6133	0.5305	0.2939	0.200	0.05312	2.301
5	500	16	95	106	82.61	76.6009	81.500	3.839	66.28435	73.95938	0.826087	0.7660	0.8150	0.6766	0.51503	0.64401	2.698



**Figure: 2** -Variation of log ( $\theta / 1-\theta$ ) with log C for *T. foenum graecum* leaves extract inhibitors for mild steel in 1.0 N HCl at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm<sup>2</sup>

## Langmuir adsorption isotherm

The process by which plant extracts function as green corrosion inhibitors in harsh settings to control the corrosion of metals and their alloys is greatly enhanced by knowledge of the adsorption isotherms (Rana *et al.*, 2017). On the surface of the metallic materials, it depicts the chemical interaction that occurs between the inhibitor molecules and the active sites. The Langmuir isotherm is the most basic isotherm model that may be used to explain the inhibitor adsorption process on the mild steel grille sheet's surface. A dimensionless separation factor (RL) from the Langmuir isotherm may be used to assess the favourability of leaf extract adsorption on the mild steel surface (Al-Turkustani *et al.*, 2011).

The surface coverage values ( $\theta$ ) according to Langmuir model for different inhibitor concentrations have been calculated. Plots of inhibitor concentrations (C) versus ( $C/\theta$ ) are shown in Figure 3 for *F. benghalensis* leaves extract and Figure 4 for *T. foenum graecum* leaves extract.

**Table: 3-** Parameters for the adsorption isotherm of *F. benghalensis* on mild steel surface in 1N HCl at 303 K temperature.

Concentration (ppm)	1 hour			6 hours			24 hours		
	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>
50	-5.81	363.6	0.95	-6.89	370.8	0.98	-7.72	409.1	0.93
100	-5.97	314.7	0.93	-6.50	354.0	0.98	-7.67	476.8	0.98
200	-4.56	299.48	0.92	-6.21	347.1	0.96	-8.50	501.5	0.95
500	-9.87	314.16	0.96	-10.07	398.2	0.97	-12.78	568.1	0.92

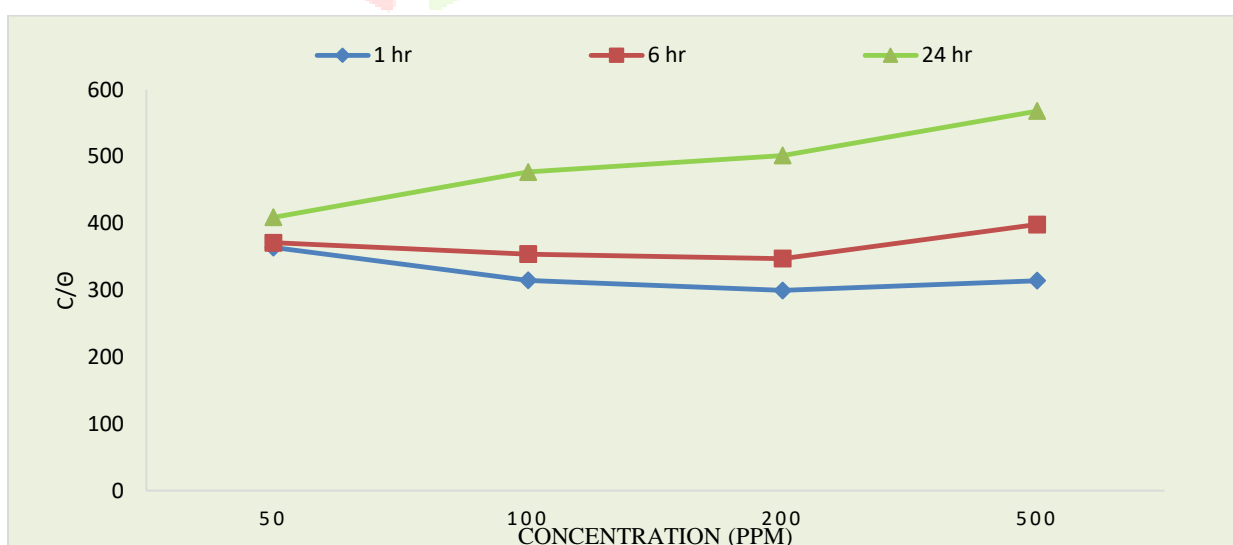
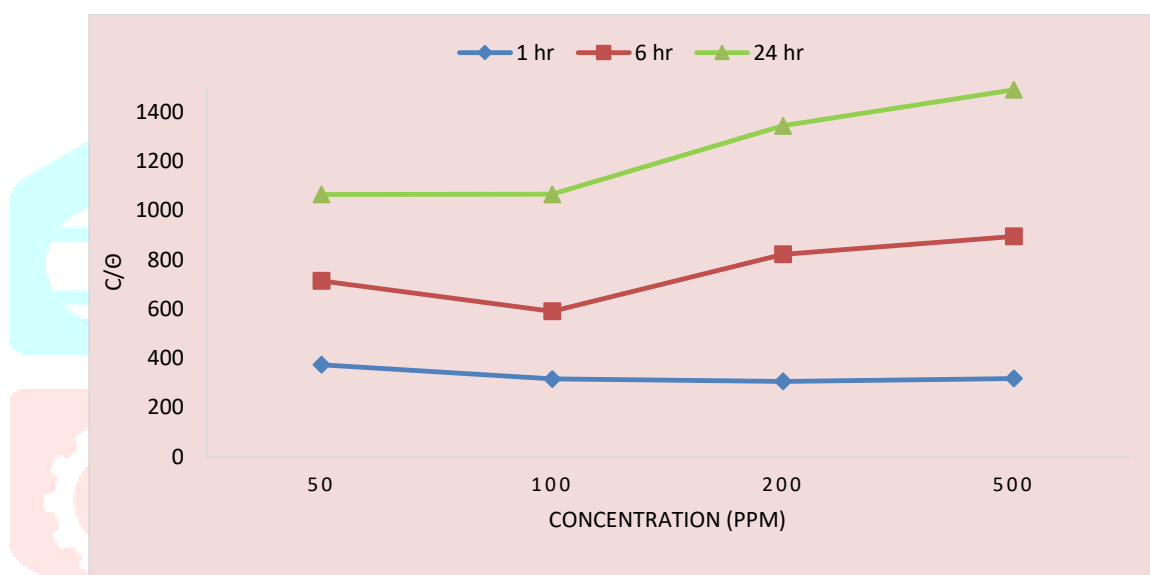


Figure: 3. Langmuir Adsorption Isotherms for the *F. benghalensis* on mild steel in HCl medium at 303K temperature.

**Table: 4-** Parameters for the Langmuir adsorption isotherm of *T. foenum graecum* on mild steel surface at 303K temperature

Concentration (ppm)	1 hour			6 hours			24 hours		
	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>	B	Kads (PPM <sup>-1</sup> )	R <sup>2</sup>
50	-5.36	373.6	0.90	-6.89	340.67	0.97	-7.07	350.66	0.99
100	-5.02	315.9	0.94	-6.50	274.95	0.99	-7.92	474.90	0.97
200	-5.78	306.3	0.95	-6.21	515.44	0.89	-8.21	522.10	0.96
500	-10.19	317.4	0.96	-10.07	577.21	0.86	12.08	595.24	0.97

Figure: 4. Langmuir Adsorption Isotherms for the *T. foenum graecum* on mild steel in HCl medium at 303K temperature.

#### Thermodynamic parameters

Result presented in the table 5 for *F. benghalensis* leaves extract & table 6 for *T. foenum graecum* leaves extract indicate that the values of free energy of adsorption for all the systems studied lie between  $-20.11$  and  $-25.12$   $\text{kJ mol}^{-1}$  signifying spontaneous adsorption of the additives via physisorption mechanism.



**Table: 5.** Activation parameters for mild steel corrosion in 1N HCl in the absence and presence of different concentrations of *F. benghalensis* leaf extracts.

Systems/concentration	$E_a$ (kJ mol <sup>-1</sup> )	$Q_{ads}$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$T\Delta S^0$ (J mol <sup>-1</sup> )	$\Delta G^0_{ads}$ (KJ Mol <sup>-1</sup> )
Blank	74.6	–	71.9	–50.3	-21.6
50	80.6	–26.5	78.0	–52.95	-25.05
100	81.9	–22.8	79.2	–54.52	-24.68
200	85.3	–26.4	82.7	–58.14	-24.56
500	93.6	–33.5	90.9	–66.22	-24.68

**Table: 6.** Activation parameters for mild steel corrosion in 1N HCl in the absence and presence of different concentrations of *T. foenum graecum* leaf extracts.

Systems/concentration	$E_a$ (kJ mol <sup>-1</sup> )	$Q_{ads}$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$T\Delta S^0$ (J mol <sup>-1</sup> )	$\Delta G^0_{ads}$ (KJ Mol <sup>-1</sup> )
Blank	74.6	–	71.9	–51.79	-20.11
50	74.8	–44.2	73.3	–48.18	-25.12
100	75.9	–50.2	77.1	–52.41	-24.69
200	79.7	–30.2	76.5	–51.89	-24.61
500	79.1	–36.5	79.7	–55.00	-24.70

The results of the thermometric method are shown in Table 7 for *F. benghalensis* leaves extract & table 8 for *T. foenum graecum* leaves extract. Higher quantities of the inhibitor (leaf extracts) decreased the rate of corrosion and weight loss, while higher temperatures enhanced it. While the efficacy of inhibition rose with increasing extract concentrations, it declined as temperatures increased. It was shown that the inhibitory efficacy decreased with temperature when leaf extract was present, which may have been caused by the physical adsorption becoming less strong.

**Table: 7.** Corrosion rate (CR) and Inhibition efficiency (IE) of *F. benghalensis* leaf extract in 1NHCl at different temperatures.

Concentration of leaf extract(ppm)	Temperature								
	303K			313K			333K		
	CR(mpy)	%IE	$\theta$	CR(mpy)	%IE	$\theta$	CR(mpy)	%IE	$\theta$
<b>Blank</b>	1458	-	-	1682	-	-	1921	-	-
<b>50</b>	324	71	0.71	458	49	0.49	1005	45	0.45
<b>100</b>	279	75	0.75	397	56	0.56	998	48	0.48
<b>200</b>	257	77	0.77	298	67	0.67	965	50	0.50
<b>500</b>	198	82	0.82	236	84	0.84	485	75	0.75

**Table: 8.** Corrosion rate (CR) and Inhibition efficiency (IE) of *T. foenum graecum* leaf extract in 1NHCl at different temperatures.

Concentration of leaf extract (ppm)	Temperature								
	303K			313K			333K		
	CR(mpy)	%IE	$\theta$	CR(mpy)	%IE	$\theta$	CR(mpy)	%IE	$\theta$
<b>Blank</b>	1458	-	-	1682	-	-	1921	-	-
<b>50</b>	337	73	0.73	464	50	0.50	1008	46	0.46
<b>100</b>	282	77	0.77	405	59	0.59	995	50	0.50
<b>200</b>	260	80	0.80	301	65	0.65	970	53	0.53
<b>500</b>	215	84	0.84	245	82	0.82	493	72	0.72

Both plants leaves extracts, as an organic inhibitor, exhibits excellent inhibition performance when exposed to a series of techniques. From the results of weight loss, Langmuir isotherm adsorption and thermodynamic parameters finally concluded that *F. benghalensis* showed better inhibition performance than *T. foenum graecum* leaves extract.

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