Tinaspora cordifolia acted as green corrosion inhibitor on mild steel in presence of 1M HCl solution

Netravati Gayakwad (netragayakwad@gmail.com)
K.L.E.I.T Hubli

Research Article

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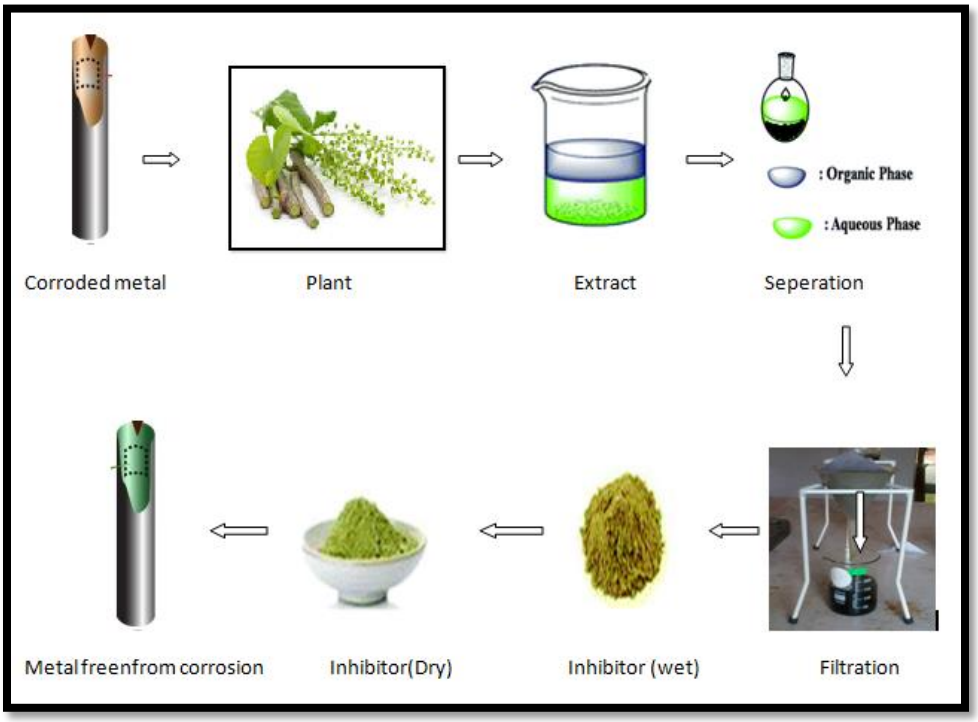
Netravati Gayakwad [a]
a- Department of chemistry , K.L.E.I.T Hubli, Karnataka, India

Abstract- Corrosion is a natural process which mainly occurs in metals. There are so many methods which inhibit the rate of corrosion. Inhibitors are organic compounds which added in a small concentration that retards the either anodic or cathodic, sometimes both. Synthetic inhibitors are non biodegradable, not easily available and toxic in nature. Considered to this point selection, some naturally available plant leaves extract that inhibit the rate of corrosion. Plant leaves extract mainly contains aromatic, aliphatic and cyclic chain compounds in their phytochemical constituents. These are abundantly easily available in nature, biodegradable, non toxic. Tinaspora cordilicia plant is rich in medicinal property as well acted as good inhibitor on mild steel in presence of 1M HCl solution. Present study investigates weight loss method at 303K.

Key words: Corrosion, Inhibition efficiency, HCl media, weight loss method



1. Introduction

Corrosion is destructive part of metal when it is reacted with an environment by either chemical or electrochemical process [1]. Corrosion is a spontaneous process which mainly occurs in metals. Metals have a different tendency to undergo corrosion. Depending on its standard oxidation potential acted more or less react with environment and undergoes corrosion [2]. Acid is mainly used in acid pickling, oil storage tanks and etc. Due to its availibity, and cost wise mild steel is one of the running metals in all industries application [3, 4]. Corrosion prevention methods are numerous not a single method is enough to apply to metals. Depending on its environment the prevention method is applied. Some are metal coatings, inorganic coating, organic inhibitor coating and cathodic metal coating. Present study is more focusing towards green inhibitors which consisting of Nitrogen, Oxygen and Sulphur in their phytochemical constituents [5, 6, 7]. Due to its abundantly available in nature, biodegrability, cost wise and non toxic property the researches has more focused on leaves extract for example.

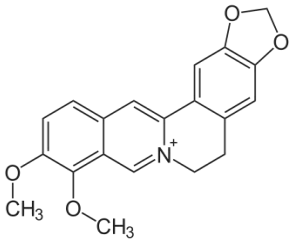
Tinospora cordifolia Family: Menispermaceae is one of the most widely used shrubs from the ancient medicinal history of Ayurveda as a medicine. Tinospora cordifolia is commonly known as Guduchi, Amrita (Sanskrit), Giloe, Gulancha (Bengali), Giloya (Hindi), Galo (Gujrati), Teppatige (Telagu), Heartleaf moonseed (Hindi). It is large deciduous climbing shrub found throughout India, and also in Sri Lanka, Bangladesh, China.

Figure 1: Image of Tinaspora cordifolia

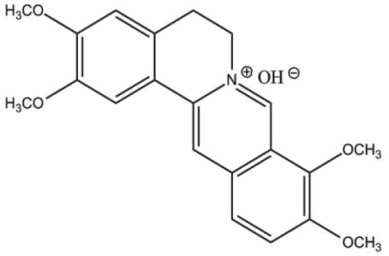
Table -1: The importance of Tinaspora cordifolia in India as medicinal plant [8]

Si No	State	Plant Part	Medicinal Uses
1	Uttar Pradesh	Juice of Stem & Root	Fever
2	Mumbai	Decoction of Leaves And Stem	Fever, Jaundice, Chroic Diarrhea, Dysentery
3	Gujarath	Juice of Root and Stem	Cancer, Dysentery, Diarrhea
4	Jammu And Kashmir	Juice of Stem	Fever
5	Bhuvaneshwar	Decoction Root	Fever
6	Panjab	Extract of Leaves	Fever
7	Jammu	Whole Plant	Bone Facture
8	Maharastra	Stem	General Debility
9	Panjab	Extract of Leaves	Karna Shula
10	UP	Decoction of Stem	Asthma
11	Rajastan	Powder seeds	Leucorrhoea
12	MP	Extract of Stem	Fever, Dysentery

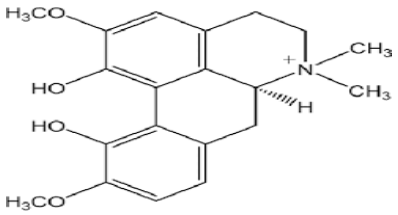
Plant leaves are rich in protein (11.2%), calcium and phosphrous. Stem contains clerodane furono diterpene glucoside camritoside, A, B, C, and D. Starch obtained from stem known as Guguchi-Satva it is highly nutritive and digestive. Gupta e al.,[9] reported the alkaloids such as chlorine, tinosorin, isocolumbin, palmatine, tetrahydropalmatine and magnoflorine present in plant extract showed protection against aflato in induced nephrotoxicity. Sharma et al., [10] studied the stem and leaves extract of the plat has shown hepatoprotective effect in swiss albino male mice against lead nitrate induced toxicity. Oral administration of plant extracts prevented the occurrence of lead nitrate induced liver damage.



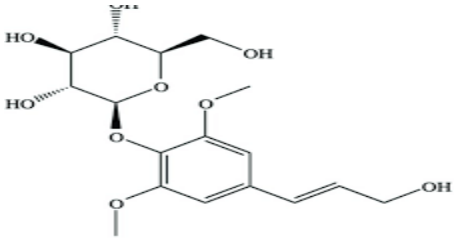
BERBERINE



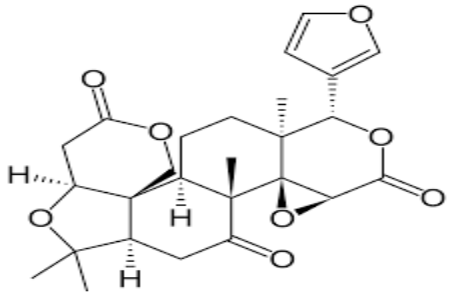
PALMATINE



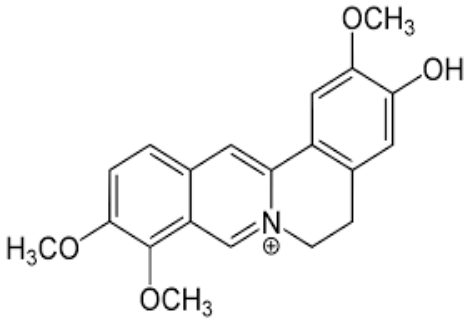
MAGNOFLORINE



SYRINGIN



FURANOLACTONE



JATRORRHIZINE

Figure 2: Tinaspora cordifolic which mainly consisting 6 group of compounds by isolation.

Table -2: List of literature reviews

SI.No	Plant Name	Author	Medium	Surface	Methods applied
1	Apple juice extract (cashew)	C A Loto and A I Mohammed [11]	HCl	Mild steel	Weight loss and Potentiodynamic polarization
2	Henna leaves	A Y El-Etre et al[12]	Neutral and alkaline solution	Mild steel	Electrochemical methods
3	Indica leave	Sanjay K Sharma and et al[13]	HCl	Mild steel	Gasometric method and electrochemical
4	Musa specimen	Eddy N O et al[14]	HCl	Mild steel	Gasometric, Electrochemical methods
5	Allamanda blanchetii	B Anand and et al[15]	H_2SO_4	Mild steel	Mass loss and
6	Tobacco leaves and kola leaf	C A Loto and et al[16]	HCl	Mild steel	Weight loss and metallographic methods
7	Potato peel	Taleb H Ibrahim et	HCl	Mild steel	Gasometric and

		al[17]			electrochemical techniques
8	Portulaca oleracea	S O Adejo et al[18]	H_2SO_4	Mild steel	Mass loss and electrochemical

2. Experimental Procedure

2.1 Materials

2.1.1 Inhibitor Preparation

Around 4-5 kg of leaves was collected around surathkal mangalore. Washed in tap water to remove unwanted matter present in leaves. Again washed with double distilled water and soak it for 1 day. The leaves were placed in grinder jar by adding 2-3 ml of distilled water along with 2-4 ml of 70% ethanol. Leaves extract were collected in separating funnel and added 5-10 ml of ether to remove chlorophyll. Next day we separated the aqueous layer from the organic layer. Solid whitish green color residue was collected from separating funnel. Whitish green residue washed with acetone and double distilled water for 2-3 times and dried under room temperature.

2.1.2 Specimen Preparation

Mild steel 3x3x0.1 cm^2 cut down and made shape properly by using polishing machine. The rust was removed by using different emery papers from harder to lower. Then washed in double distilled water and placed in desiccators for experimental use.

2.1.3 Electrolyte Preparation

1M Solution of HCl solution were prepared by taking 86.6 ml to conical flask and by adding double distilled water up to the mark.

3. Methods

3.1 Weight loss studies

The polished, degreased specimens of mild steel is weighed and immersed in 150ml beakers containing 100ml 1M HCl. It is followed by measurement by weight loss once every 24 hour for 5 days. The later measurement is done after the specimen is cleaned in distilled water, rinsed in acetone and dried. The experiment is repeated with different known amount of inhibitor in the 1M hydrochloric acid medium.

The percentage of inhibition efficiency was evaluated from,

weight loss measurement using the formula

$$IE\% = \frac{W_o - W_i}{W_o} \times 100 \text{ ----------[19]}$$

Where IE is inhibition efficiency, W_o & W_i is weight loss in 'g'. W_o is absence of inhibitor; W_i is presence of inhibitor.

Corrosion rate

$$w = \frac{m1 - m2}{S.t}$$

m1 = mass of specimen before corrosion

m2 = mass of the specimen after corrosion

S = total area of the specimen

t = corrosion time

w = corrosion rate

The degree of surface coverage θ was calculated using the following equation

$$\Theta = 1 - \frac{Winh}{W\ corr}$$

3.2 Polynomial regression analysis of corrosion behavior

polynomial regression models are usually fit using the method of least squares. polynomial regression is a form of regression analysis in which the relationship between the independent variable x and the dependent variable y is modeled as an nth degree polynomial in x.

3.3 Adsorption isotherm

Inhibitors protect metals from rust by deposition onto the surface by forming a thin deposition film. The efficiency of an inhibitor is greatly dependent on the extent of adsorption of the inhibitor molecules on the metal surface. The nature of rusting inhibitor has been deduced in terms of the adsorption characteristics of the inhibitor. The establishment of isotherms that describe the adsorption behavior of the inhibitor is important as they can give important clues about the nature of metal inhibitor interaction.

Table -3: List of adsorption isotherms

Name	**Formula**	**Graph plotted Y axis ≪ X axis**
Langmuir	$\frac{C}{\theta} = \frac{1}{K} + C$	C/θ Verses C
Temkin	-2aθ = ln KC	θ Verses ln C
Frumkin	$\log\frac{\theta}{C(1-\theta)} = \log K + g\theta$	$\log\frac{\theta}{C(1-\theta)}$ Verses θ

4. Result and Discussion

4.1. Tinospora Cordifolia

Mild steel specimen soaked in 1M HCl solution in presence and absence of numerous dosage 0.01g/L, 0.02g/L,0.03g/L, 0.05g/L, 0.10g/L, 0.20g/L, 0.30g/L, and 0.40g/L weight loss was recorded at every 24h for the immersion time of 5 days. The corrosion efficiency of inhibition and corrosion rate was calculated and taken down in Table 4 at 303K.

Effect of Inhibitor concentration

The inhibition efficiency of various concentrations of Tinospora cordifolia on mild steel in 1M HCl is obtained from mass loss measurements and presented in the Tables-4.

Inspection of Table-4 reveals that the inhibition efficiency of Tinospora cordifolia rises with rising in concentration and reached maximum inhibition efficiency from 49.8% to 85.57% at 0.01 g/L to 0.40 g/L concentration of the extract and it is almost

constant above this concentration at longer immersion time.

Effect of Immersion

The variation of inhibition efficiency of Tinospora cordifolia with immersion period is given in Table- it is seen that the inhibition efficiency increased with immersion time and attained a maximum at 120 h and thereafter decreased. An excellent inhibition efficiency of 85.57% is obtained at 120 h. The corrosion rate of mild steel in the absence and in the presence of various concentrations of Tinospora cordifolia extract has been calculated from weight loss measurements. The graph of weight loss in g against time in days, and inhibition efficiency against time in days is reported in Figure -3a & 3b

The results show that Tinospora cordifolia extract acted as good inhibitor in 1 M HCI. The increase in inhibition efficiency with the period of immersion may be due to the increase in adsorption of phytochemical constituents of the extract on the surface of mild steel.

Table-4: Weight loss method of Tinospora cordifolia in 1M HCl solution on mild steel surface presence and absence of inhibitor.

Con. Of inhibitor in g/L	Weight loss in g					CR	I.E %				
	24 h	48 h	72 h	96 h	120h		24 h	48 h	72 h	96 h	120h
0	0.7427	1.7562	3.0171	4.5058	6.1993	0.1660	**14.94**	29.93	38.95	43.92	49.80
0.01	0.6317	1.2316	1.8417	2.527	3.1117	0.1014	84.45	87.11	73.49	69.75	68.88
0.02	0.1159	0.2264	0.7998	1.363	1.9288	0.0766	64.90	57.80	63.70	36.02	34.76
0.03	0.3581	0.7411	1.0953	1.6231	2.1547	0.0484	79.38	87.20	90.20	91.70	92.39
0.05	0.1531	0.2245	0.2951	0.3733	0.4712	0.0278	94.81	92.73	90.66	88.23	86.35
0.10	0.0933	0.1587	0.3055	0.5636	0.8461	0.0391	83.58	85.36	84.43	83.90	83.38
0.20	0.1419	0.3208	0.6015	0.9066	1.3030	0.0340	63.85	67.35	70.60	73.17	75.40
0.30	0.2685	0.5733	0.8872	1.2073	1.5216	0.0321	87.10	88.90	87.66	86.02	85.57
0.40	0.0925	0.1947	0.3722	0.6299	0.8999	0.0226	**14.94**	29.93	38.95	43.92	49.80

Figure 3. a Weight loss of mild steel against time in days and inhibitor concentration 0.01-0.40g/L

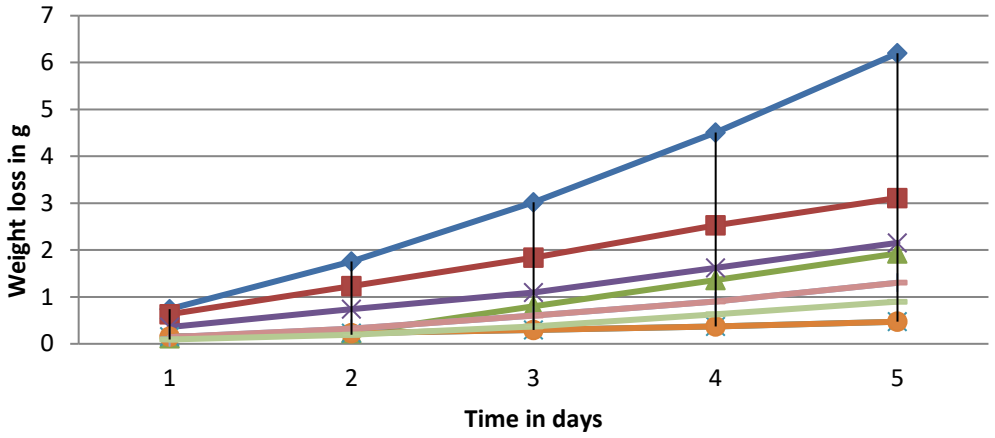
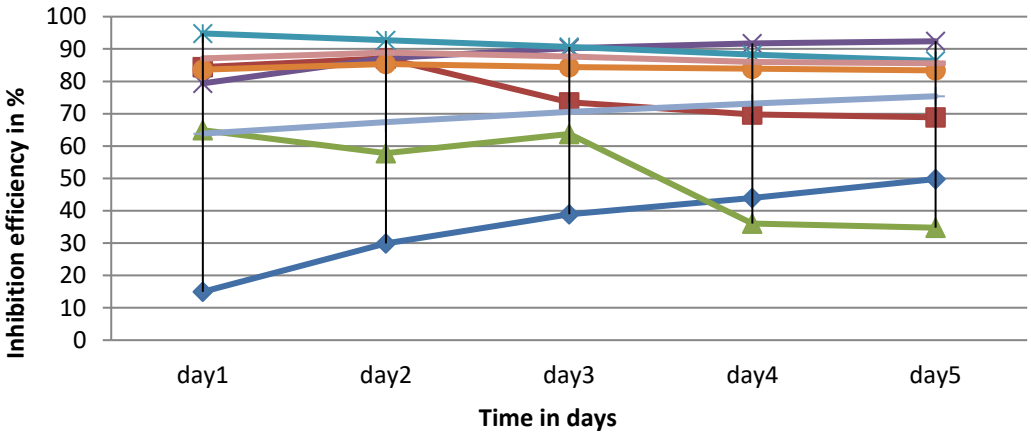


Figure 3 b.Inhibition efficiency of Tinospora cordifolia against concentrtion of inhibitor from 0.01 to 0.40 g/L from day 1 to day 5



4.1.1 Polynomial regression analysis of corrosion behavior

From the metal weights the average decaying rates were calculated using the following formula.

$$w_5 = w_0(1-r)^5$$

$$r = \left(1 - \left(\frac{w_5}{w_0}\right)^{\frac{1}{5}}\right)$$

To explain the relation of inhibitor concentration and average corrosion rate, the

least square method is used to find the equation which has minimum deviation from the curve obtained. It was found that polynomial regression model degree 5 best fit to the data and equation is given by

$$Y = 1.618e^{-1} - 6.054e^{-2}x + 9.181e^{-3}x^2 - 5.753e^{-4}x^3 + 1.562e^{-5}x^4 - 1.522e^{-7}x^5$$

A graph plotted average rate of corrosion against inhibitor concentration is as shown in Figure 4 this model explains the 98.38% of the variation in average corrosion rates.

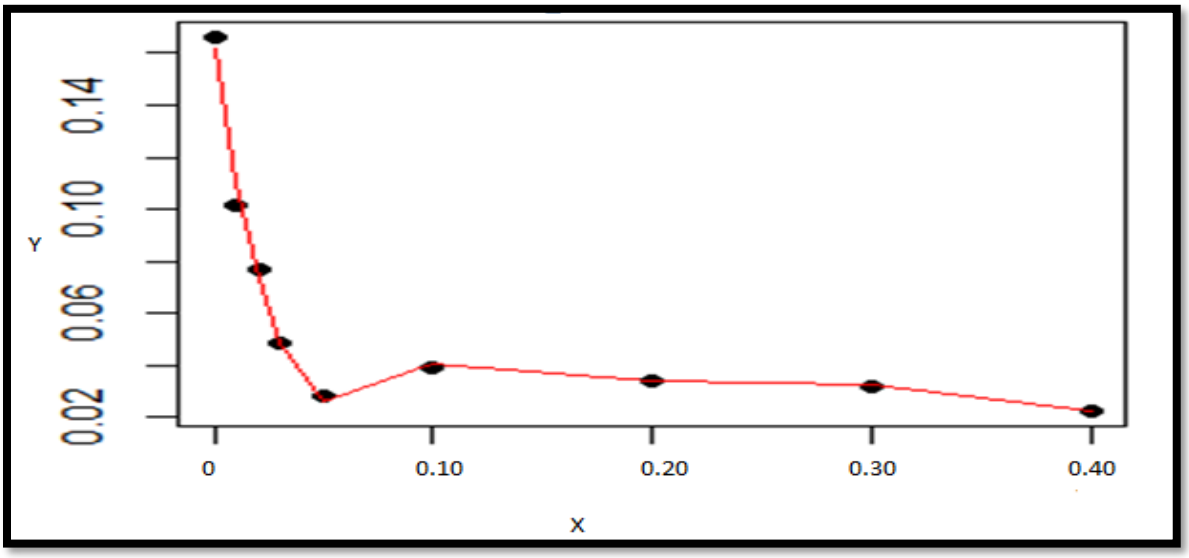


Figure 4: Polynomial regression of Tinaspora cardifolia leaves extract of average rate of corrosion with inhibitor. (x-axis concentration of inhibitor & y-axis average corrosion rate)

4.1.2 Adsorption isotherm

Adsorption isotherm gives knowledge about interaction of adsorbed molecule with surface of inhibitor. Adsorption may take place on surface of mild steel either physiorption or chemisorptions it mainly depends on the molecular structure present in the inhibitor and also it depends on the electrolyte, nature of metal and type of inhibitor used. The plots of C/θ against C yield straight line with approximately unit slope as shown in Figure-5, indicating that.

inhibitor under study obeys Langmuir adsorption isotherm

$$K_{ads} = \frac{1}{55.5} \exp \frac{\Delta G}{RT}$$

Where,

ΔG = -RT ln (55.5 K_{ads})

Where R is the gas constant T is absolute temperature. The intercept permits the calculation of equilibrium constant K_{ads} and value were tabulated in Table-5. The negative value of ΔG was -23.5980 kJ/mol

showed that the adsorption of inhibitor molecule on the surface is spontaneous.

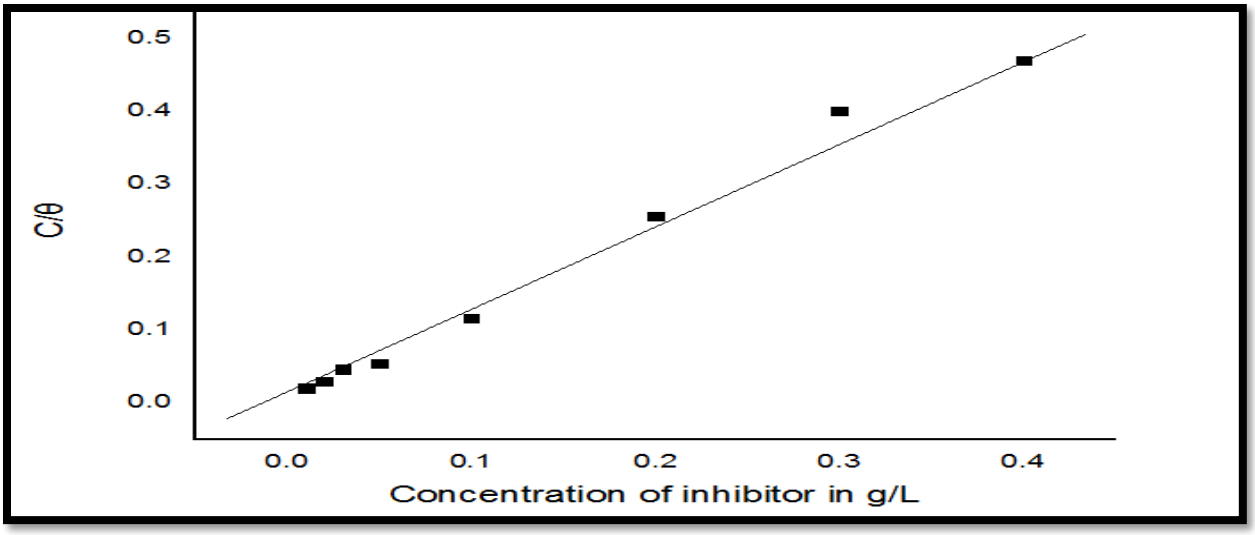


Figure 5: Langmuir adsorption isotherm of Tinaspora cardiofolia leaves extract

Table 5- Adsorption isotherm parameters of Tinaspora cordifolia leaves extract.

Con. of inhibitor in g/L	Corrosion rate	θ	C/ θ	Slope	Intercept	K_{ads}	R^2	ΔG(kJ/mol)
0.01	**0.836**	0.490	0.020	1.218	0.004	212.760	0.992	**-23.598**
0.02	0.518	0.68	0.029					
0.03	0.579	0.650	0.046					
0.05	0.126	0.920	0.054					
0.10	0.227	0.860	0.116					
0.20	0.35	0.780	0.256					
0.30	0.409	0.750	0.400					
0.40	0.241	0.850	0.470					

4.4 Adsorption mechanism of green corrosion inhibitor

Adsorption mechanism is usually explained through the help of adsorption isotherms Langmeir, Frumkin, Temkin, Freundlich, etc. The adsorption of inhibitor on solid surface mainly include adsorption mode, chemical and electronic characteristic of the inhibitor, temperature, nature of electrolyte medium. The adsorption of inhibitor on corroded metal surface is mainly physical or chemical adsorption isotherm. Physical adsorption isotherm occurs due to electrostatic interaction between charged centers of molecule and charged metal surface which results in a dipole interaction of the molecule and metal surface [20]. Chemical adsorption isotherm is a process which involves the transfer or sharing of electron from inhibitor to the

metal surface to form a coordinate bond and bonding strength of chemisorptions was much larger than physical adsorption. The –ΔG value for chemisorptions was found to be more than 40 kJ/mol and below this value physiorption. The ΔG value for Tinaspora cordifolia, Carica papaya, and Wedilia tricobata are less than -20 kJ/mol, hence also plant leaves inhibitors acted as physiorption and reaction is spontaneous.

5. Conclusion

Tinospora cordifolia acted as a ayurvedic medicine in India, China, Sri Lanka, Bangladesh and other countries as well it also shows a property of natural corrosion inhibitor on mild steel. As the concentration of inhibitor increasing, the inhibition efficiency also increases. For Tinaspora cordifolia showed 85.57% of inhibition efficiency at 30.0 g/L. Plant leaves extract which obeys Langmuir adsorption isotherm and showing ΔG value below -20kJ/kg which reports physical adsorption.

Ethical approval

-Not applicable

Competing interest

-Not interested in financial interest

Authours Contribution

-Not applicable

Funding

-No funding received

Availibility of data and materials

-No data has been accessed

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