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Inhibitive action of aqueous extract of *Holoptelea integrifolia* leaves for the corrosion of mild steel in 1N HCl solution

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ABSTRACT

The inhibitory effect of aqueous extract of leaves of Holoptelea Integrifolia (HI) plant on the corrosion of mild steel in 1N HCl was investigated by using traditional weight loss method and electrochemical method. Organic moieties present in the extract are found responsible for effective performance of the inhibitor which was well supported by FTIR studies. Potentiodynamic polarization curves revealed that the inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 98.45 % can be obtained. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract. Temperature studies revealed that the the inhibition efficiency decrease with increasing temperature which suggests that it follows physisorption mechanism. Surface coverage values were tested graphically for suitable adsorption.

Keywords: Mild Steel, EIS, SEM, Acid Corrosion, Polarization.

INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion can be controlled by suitable modification of the environment which in turn retards or completely stop the anodic and cathodic reactions or both. This is achieved by the use of inhibitor [1-5]. Hence corrosion inhibition in acidic media becomes a necessity. The role of an inhibitor is to form a barrier of one or several molecular layer against acid attack. This protective action is often associated with chemical and/or physical adsorption involving in the change of the adsorbed substance and transfer of change from one phase to the other. Sulphur and /or nitrogen containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitor. These inhibitors have also found useful application in the formulation of primer and anti-corrosive coating. Organic compounds have widely been tried as the corrosion inhibitor for metals and alloys. The corrosion inhibition of mild steel in acidic media in the presence of various organic and inorganic compounds has been reported [6-8]. Many synthetic compounds offer good anticorrosive action; but most of them are highly toxic to both human beings and environment. In recent years, plant extracts and oils have become important as an environmentally acceptable, readily available and renewable source of material for wide range of corrosion prevention. Attention has been focused on the corrosion inhibiting properties of plant extracts because plant extracts serve as incredibly rich source of natural chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable sources of materials and can be extracted by simple procedures [9-10].

Many plant extracts such as Madhuga longifolia (Sivakumar P R 2015), have been studied for the corrosion inhibition of mild steel in acidic media. The gum extract of Raphia hookeri (Umoren, 2009) have also been analysed for corrosion inhibition properties. The present research work aims at establishing the effectiveness of aqueous plant extract as corrosion inhibitor in 1N HCl media using weight loss measurement at various time and temperature, electrochemical techniques. The influence of temperature on adsorption and inhibition efficiency has been studied.

MATERIALS AND METHODS

2.1 Preparation of mild steel specimen
Mild steel strips (C- 0.030 %, Mn- 0.169 %, Si- 0.015 %, P- 0.031 %, S - 0.029 %, Cr- 0.029 %, Ni- 0.030 %, Mb-0.016 %, Cu- 0.017 % and the remainder Fe) of dimension 4 cm x 2 cm x 0.1cm were polished to a mirror finish with the emery sheet of various grade and degreased with acetone.

2.2 Preparation of the plant extract
The leaves of the medicinal plants HI were dried and ground well into fine powder. 10 g of sample was refluxed in 150 ml distilled water and kept overnight. The aqueous solution was filtered and volume was made up to 500 ml using double distilled water. This extract was used a corrosion inhibitor in the present study.

2.3 Weight loss method
The polished mild steel specimens with uniform size were tied with threads and immersed in 200 ml test solution in the absence and presence of various concentration of the inhibitor for 24 hours. The mild steel specimens after 24 hours were washed, dried and the weight loss was calculated.

$$\mathrm{CR\ (mmpy)} = \frac{\mathbf{K} \times \mathrm{Weight\ Loss}}{\mathrm{D \times A \times t\ (in\ hours)}} \qquad (2)$$

Where, K = 8.76 x 10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.
The inhibition efficiency (%) was calculated using equation (3)

$$\mathrm{IE\ \%} = \frac{W_0 - W_i}{W_0} \mathrm{X} 100 \qquad (3)$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor respectively.

2.4 Potentiodynamic polarization methods
Potentiodynamic polarization measurements were carried out using CHI660E electrochemical analyzer. Experiment were carried out in a conventional three electrode cell assembly with mild steel specimen of 1cm^2 as working electrode, a rectangular Pt foil as counter electrode, and the standard calomel electrode as reference electrode. The polarization was carried from a cathodic potential of -800 mV (vs SCE) to an anodic potential of -200 mV (vs SCE) at a sweep rate of 1 mV per second.

$$\mathrm{IE\ \%} = \frac{I_{Corr} - I_{*Corr}}{I_{Corr}} \times 100 \qquad (4)$$

Where, I_{corr} and I_{*corr} are corrosion current in the absence and presence of inhibitors.

2.5 Electrochemical impedance method
The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and the imaginary part (Z") were made as plot. Then, the R_{ct} values are calculated using the following expression:

$$C_{dl} = \frac{1}{2\pi} f_{max} R_{ct} \qquad (5)$$

Where R_{ct} is charge transfer resistance, and C_{dl} is double layer capacitance.

$$\mathrm{IE\%} = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \qquad (6)$$

Where, R_{ct} and R^0_{ct} are the charge transfer resistance values in the inhibited and uninhibited solution.

2.6 Scanning electron microscopy (SEM)
The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology.

RESULTS AND DISCUSSION

3.1 Weight loss method

The weight loss studies were done in 1N hydrochloric acid in the absence and presence of various concentration of the plant extracts ranging from 5 to 20 ppm. The corrosion parameters obtained in the weight loss method are given in Table 1. It was observed from the table that the increase in concentration of HI leave extract on the corrosion rate of mild steel in 1N HCl solution was decreased and the inhibition efficiency increased to 86.59% at 15 ppm.

Table 1. Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Conc. of HI leaves Extract (ppm)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition Efficiency (%)
Blank	0.0470	206.47	*
05	0.0118	026.41	74.89
10	0.0103	022.57	78.08
15	0.006	020.00	86.59
20	0.0084	027.77	81.48

3.2 FTIR Measurement

FTIR spectra of the HI leaves extract is shown in Fig. 1. It was observed from the figure that the broad peak obtained at 3395.18cm-1 can be assigned to N-H or O-H stretching. C-H stretching was observed at 2918.35 cm-1. Other strong peak obtained at 1880.83 cm-1 correspond to C=O (may be aldehyde or ketone). Strong peaks obtained at 1632.46cm-1 and 1629.09cm-1 were due to C=C or C=N stretching or N-H bending vibration. Absorption band at 1414.03cm-1 can be assigned to C-H bending in CH3 or O-H bending vibration. Peaks observed at 1380.14cm^{-1}, 1228.34cm^{-1} and 1102.27cm^{-1}was due to C-N and C-O stretching vibration. Few weak peaks can also observed at 1228.34cm^{-1} which correspond to C=C stretching vibration of aromatic ring.

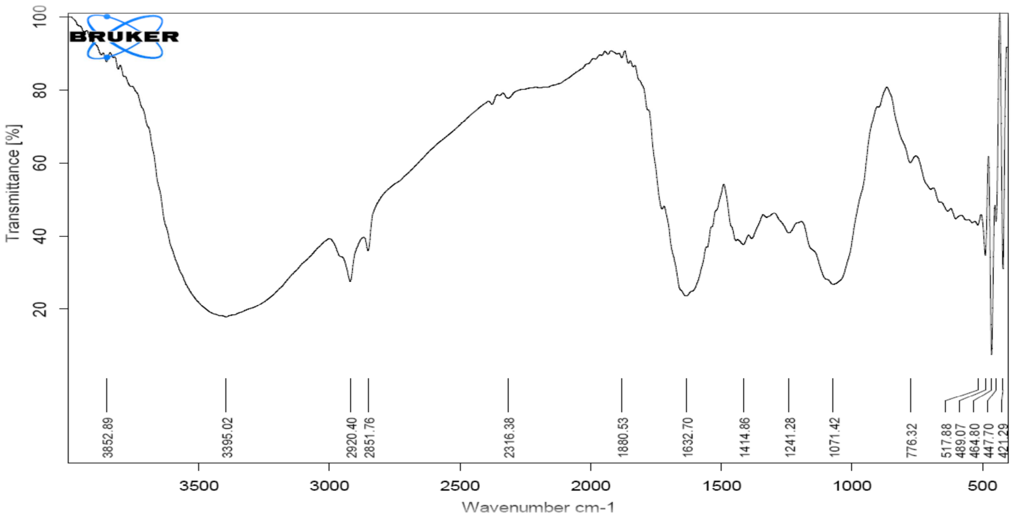


Fig. 1 FTIR Spectra of *Holoptelea Integrifolia* leaves Extracts

3.3 Potentiodynamic polarization methods

The electrochemical parameter like corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes (b_c), anodic Tafel slope (b_a) and percentage of inhibition efficiency (IE%) for mild steel in the absence and presence of various concentrations of HI extract in 1N HCl is given in Table 2 and their polarization curves are shown in Fig. 2. It is noted from the table that the addition of green inhibitor decreases the dissolution rate of mild steel in 1N HCl acid media.

Table 2. Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Conc. of HI leaves extract (ppm)	E_{corr}/ (mV/ SCE)	I_{corr}/ (mA/cm^2)	b_c (mV/dec.)	b_a (mV/dec.)	LPR Ohm*cm^2	IE (%)
Blank	-0.471	4.706×10^{-3}	209	153	8.2	*
5	-0.468	1.067×10^{-3}	160	115	27.3	77.32
10	-0.475	7.255×10^{-4}	165	90	35.0	98.45
15	-0.476	3.273×10^{-3}	131	100	76.4	93.05
20	-0.465	6.079×10^{-4}	146	96	40.0	87.08

The corrosion current density values decreased considerably for green inhibitor in the acid media. However, the shift in the values of corrosion potential (E_{corr}) for HI leaves extract is not significant (31). This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors.

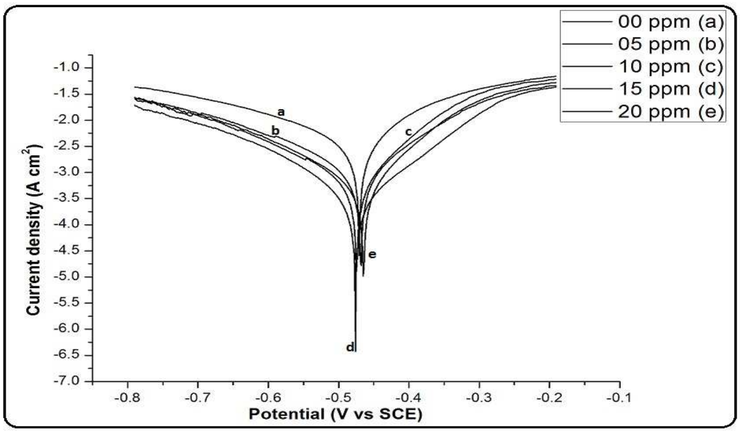


Fig 2. Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Holoptelea Integrifolia* extracts of leaves

3.4 Electrochemical impedance methods

The Nyquist plots for mild steel in 1N HCl with different concentration of HI leaves extract are shown in Fig.3 and EIS parameters derived from these investigations are given in Table 3. It was observed from Fig. 3, the obtained impedance diagrams were almost in a semi-circular appearance, indicating that the charge transfer process mainly controls the corrosion of mild steel.

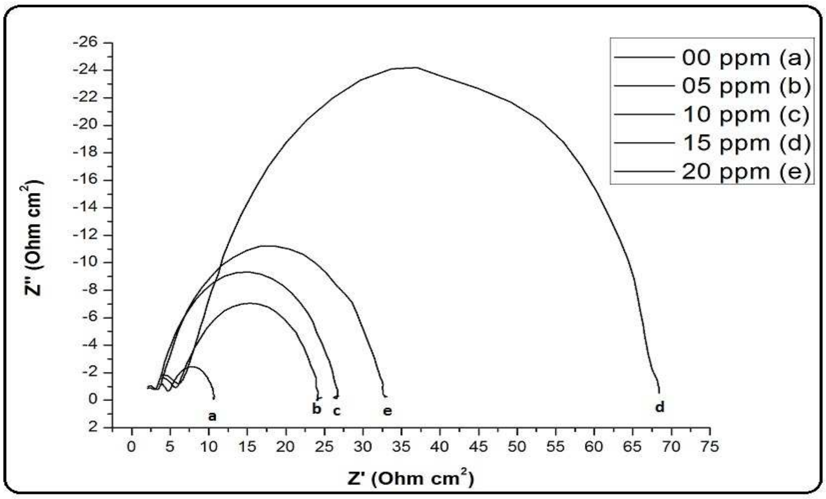


Fig 3. Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Holoptelea Integrifolia* leaves extract

Values of double layer capacitance were also brought down to the maximum extent in the presence of inhibitor and the decrease in values of C_{dl} follows the orders similar to that obtained I_{corr} in this study. The decrease in C_{dl} shows that the adsorption of this inhibitor takes places on the metal surface in acidic solution [33-37].

Table 3. Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of inhibitor

Conc. HI leaves Extract (ppm)	R_{ct} (ohm cm^2)	C_{dl} (µF/cm^2)	IE (%)
Blank	8.937	7.266x10-3	*
5	22.713	1.002x10-3	60.65
10	24.901	6.870x10-4	64.10
15	65.854	9.830x10-5	86.42
20	31.568	4.460x10-4	71.68

3.5 Phytochemical screening method

Phytochemical screening of the aerial parts of plant's powder (aqueous) extract was tested in order to find the presence of various chemical constituent included alkaloids, carbohydrates, proteins, saponins, triterpenoids and tannins [32] and the results are listed in Table 4.

Table 4. Phytochemical screening test for extract of Holoptelea Integrifolia

Phytochemical test	Aqueous extract
Alkaloids	+
Xanthopretins	+
Diterpenes	-
Saponins	+
Phytosterols	-
Tannins	+
Flavanoids	+
Phenol	+
Steroids	+
Quionones	-

(+) Presence (-) Absence

3.6 Scanning Electron Microscopy (SEM)

Surface analysis of metals using Scanning electron microscopy image has become an essential tool to study the surface morphology of corroded and uncorroded metal. To confirm interaction of the inhibitor with the metal surface, SEM images were recorded for the mild steel specimens exposed to 1N HCl in the absence and presence of optimum concentration of extract are shown in Fig. 4a and 4b. Examination of Fig. 4a revealed that the specimen immersed in 1 N HCl was rough and highly damaged due to the attack of aggressive acids. Fig. 4b clearly showed that the smooth mild steel surface was covered with the protective layer formed by inhibitor, which prevents the metal from further attack of acid medium thus inhibiting corrosion [38-44].

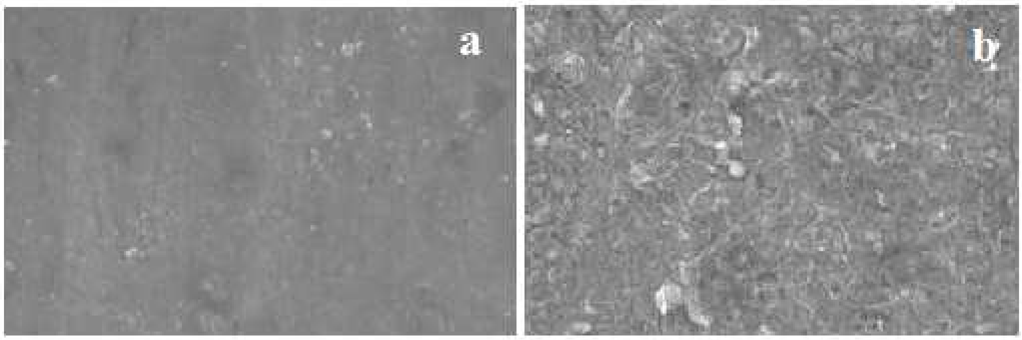


Fig 4. SEM image of the surface of mild steel after immersion for 24 hours in 1N HCl solution in the absence (4a) and in the presence (4b) of optimum concentration of the HI plant Leaves extracts

3.7 Effect of immersion time

The variation of inhibition efficiency for different concentration of leaves extract of HI was listed in the Table 5. Maximum inhibition efficiency for 1N Hydrochloric acid was found to be 92.73 % with 15 ppm concentration of the inhibitor at 24 h.

Table 5. Inhibition efficiency at various immersion times

Conc. of HI leaves extract (ppm)	IE (%)				
	1h	3h	5h	7h	24h
5	66.37	60.15	70.34	80.10	83.70
10	78.89	62.39	76.72	83.36	83.72
15	88.92	72.97	82.14	89.75	92.73
20	82.56	70.16	58.15	65.00	68.82

3.8 Effect of temperature

To assess the effect of temperature on corrosion and corrosion inhibition process, thermostat experiments were performed at different temperature (303-343K) in the absence and presence of various concentration of the inhibitor during 3 hours of immersion. The results are given in Table 6.

Table 6. IE at various temperatures

Conc. of HI leaves extract (ppm)	IE (%)				
	303K	**313K**	**323K**	**333K**	**343K**
5	75.64	72.62	52.75	50.17	43.16
10	84.51	79.39	54.14	55.15	52.94
15	89.56	81.50	60.12	60.07	57.10
20	91.02	90.48	72.18	64.17	62.45

3.9 Adsorption isotherm

As organic compound in the inhibitors protect the metal against corrosion by their adsorption onto metal surface, the adsorption behaviour of inhibitor is an important part of study. The phenomenon of interaction between the metal surface and inhibitor can be better understood in term of adsorption isotherm. The plot θ vs Ln C gave a straight line indicating that the inhibitor under the study obeys Temkin adsorption isotherm. This may also infer that there is a molecular interaction among the adsorption particles and metal surface.

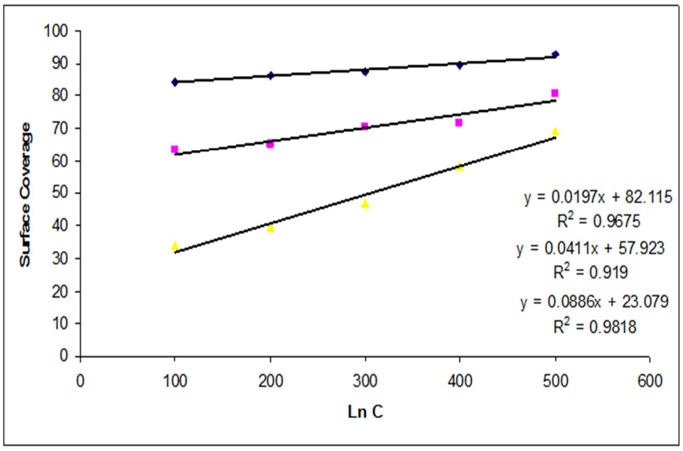
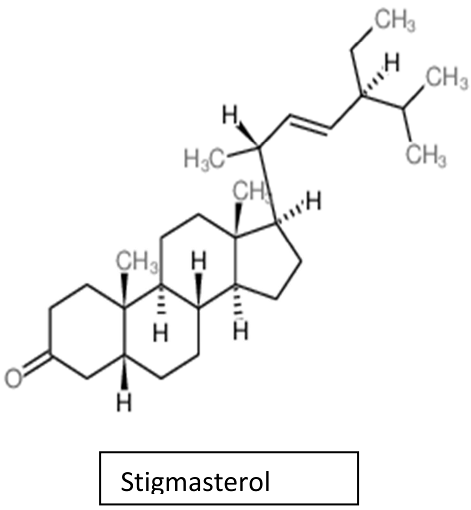
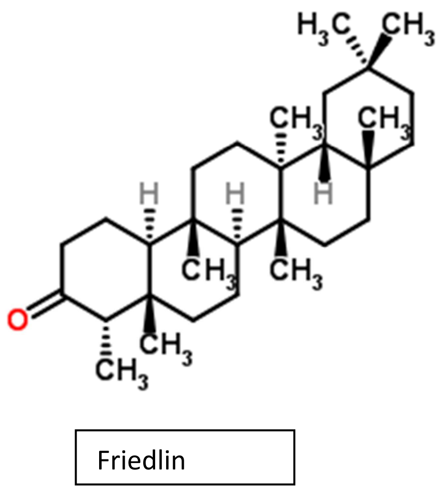


Fig 5. Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of the extract

3.10 Mechanism of inhibition





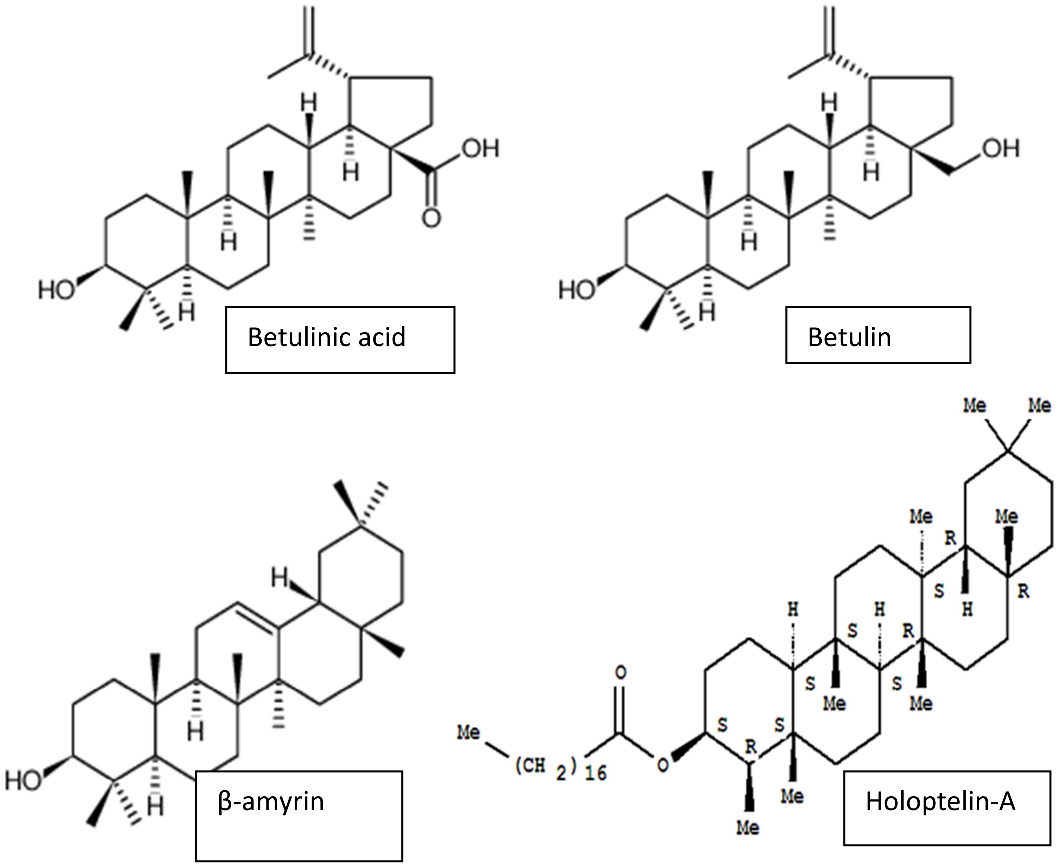


Figure 6. Phytoconstituents isolate from HI plants

The probable mechanism of inhibition can be explained on the basis of adsorption process and the structure of the constituents present in the HI extracts. The main constituent of HI leaves extract is (Holoptelin –A, Friedlin, β-amyrin, betulin, betulinic acid) [45-51] whose structure are given Fig. 6 having multiple bond through which they get adsorbed on the metal surface. This depends on the chemical composition and structure of the inhibitor, the nature of metal surface, and the properties of the medium. Structural and electronic parameters like functional group, steric and electronic effects may also be responsible for inhibition efficiency of any inhibitor that was the adsorption mechanism. The compounds have to block the active corrosion sites on the metal surface and hence the adsorption occurs by the bonding of the free electron of inhibitor with the metal. The HI extracts may also constitute heterocyclic compounds such as imidazole, pyrrole, pyridine ring saponins, tannins, alkaloids, flavonoids, glycosides and steroids etc. These compounds possess hetero atoms such as Oxygen and Nitrogen which strengthen their adsorptive property over mild steel surface. These organic molecules get physisorbed on the metal surface forming a protective film and hence the anti – corrosive behaviour [52-59].

CONCLUSION

The results obtained showed that HI leaves extract is a good corrosion inhibitor for mild steel under acidic condition. The maximum inhibition efficiency was found to be 98.45 %. It was also found that the inhibitor worked as a mixed type inhibitor retarding both anodic and cathodic reactions. Surface images of the mild steel surface clearly showed that HI leaves extract inhibited corrosion of mild steel by getting adsorbed on the metal surface. The adsorption fits well to the Temkin adsorption isotherm. The results suggest that HI leaves is a corrosion inhibitor for mild steel in HCl and they can be used to replace toxic and non-bio gradable inhibitors.

REFERENCES

[1] Srikanth A P, Nanjundan S, Rajendran N. *Prog. Org. Coat.,* **2007,** 60: 320-327
[2] Hosary A A, Saleh R M, Eldin A M S. *Corr, Sci.,* **1972,** 12: 897–904
[3] Shymala M, Kasthuri P K. *Int. J. Corros.,* **2011,** 129647: 1-11.
[4] Karuppusamy M, Sivakumar P R, Perumal S, Elangovan A, Srikanth A P. *J. Env. Nano.,* **2015,** 4(2), 09-15

[5] Srikanth A P, Raman V, Tamilselvi S, Nanjundan S, Rajendran N. *Anti-corrosion Methods Mat.*, **2008,** 55(1): 3-9
[6] Sivakumar P R, Srikanth A P. *Int. j. phy. app. Sci.*, **2016,** 3 (1): 10-20
[7] Loto C A, Mohammed A I. *Corros. Prevent Control.*, **2000,** 47: 5056–5063
[8] Srikanth A P, Sunitha T G, Raman V, Nanjundan S, Rajendran N. *Mater. Chem. Phy.*, **2007,** 103: 241-247
[9] El-Etre A Y. *Corros. Sci.*, **2003**, 45: 2485–2495
[10] Bruneton J. Tec & Doc-Edition, Medicinales Internationales, 4th ed. Paris; France: **2009**
[11] Sivakumar P R, Srikanth A P. *Int. J. Eng, Sci. Comp.*, **2016,** 6 (8): 2744-2748
[12] Vishalakshi K, Sivakumar P R, Srikanth A P. *Int. Org. Sci. Rese. J. App. Chem.*, **2016,** 9(9): 50-55
[13] Ajmal M, Mideen AS, Quraishi MA. *Corros Sci.*, **1994**, 36: 79–84
[14] Srikanth A P, Sunitha T G, Nanjundan S, Rajendran N. *Prog. Org Coati.*, **2006,** 5: 120-125
[15] Verma S A, Mehta M N. *Trans. Soc. Advan. Electrochem Sci Technol.*, **1997,** 32: 89–93
[16] Obot IB. Umoren SA, Obi-Egbedi NO. *J. Mater Environ. Sci.*, **2011,** 2: 60–71
[17] Al-Sehaibani H. *Material wissenschaft und Werkstofftechnik.*, **2000,** 31: 1060–1063
[18] Lebrini M, Robert F, Roos C. *Int. J. Electrochem Sci.*, **2010,** 5: 1698–1712
[19] Sivakumar P R, Karuppusamy M, Perumal S, Elangovan A, Srikanth A P. *J. Env. Nano.*, **2015,** 4(2): 31-36
[20] Davis GD. DACCO SCI Inc. Columbia Md; USA: **2000**.
[21] Abiola O K. *J. Corros .Sci. Eng.*, **2006,** 5: 10-17
[22] James A O, Ekpe E O. *Int. J. Pure Appl. Chem.*, **2002,** 35: 10-13
[23] Lebrini M, Robert F, Roos C. *Int. J. Electrochem. Sci.*, **2011,** 6: 847–859
[24] Sivakumar P R, Vishalakshi K, Srikanth A P. *J. Appli. Chem.*, **2016,** 5(5),
[25] Ebenso E E, Eddy N O, Odiongenyi A O. *Afr. J. Pure Appl. Chem.*, **2008,** 2: 107–115.
[26] Mejeha I M, Uroh A A, Okeoma K B, Alozie G A. *Afr. J. Pure Appl. Chem.*, **2010,** 4: 158–165
[27] Sivakumar P R, Karuppusamy M, Vishalakshi K, Srikanth A P. *Der Phar. Chem.*, **2016,** 8(12): 74-83
[28] El-Etre A Y, Abdallah M, El-Tantawy Z E. *Corros. Sci.*, **2005,** 47: 385–395
[29] Oguzie E E. *Mater.Chem. Phys.*, **2006,** 99: 441–446
[30] Gunasekaran G, Chauhan L R. *Electrochimica Acta.*, **2004,** 49: 4387–4395
[31] Orubite K O, Oforka N C. *Mater. Lett.*, **2004,** 58: 1768–1772
[32] Li Y, Zhao P, Liang Q, Hou B. *Appl. Surf. Sci.*, **2005,** 252: 1245–1253
[33] Quraish M A, Yadav D K. Corrosion and its control by some green inhibitor in Proceedings of the 14th National Congress on Corrosion Control: **2008**.
[34] Edeoga H O, Okwu DE, Mbaebie B O. *Afr., J. Biotech.*, **2005,** 4: 685-688
[35] Ade R, Rai M K. *Biodiversitas.*, **2009,** 10: 210-214
[36] Alagesaboopathi C. *J. Microbiol.*, **2011,** 5: 617-621
[37] Hemaiswarya S, Raja R, Anbazhagan C, Thiagarajan V. *Pak. J. Bot.*, **2009,** 41: 293-299
[38] Rehanabanu R, Nagarajan N. *Int. Res. J. Pharm.*, **2011,** 2: 139-142
[39] Mathur A, Verma S K, Singh S K, Mathur D, Prasad GBKS, Dua V K. *Rec. Res. Sci. Technol.*, **2011,** 3: 40-43
[40] Kala C P. *Int. J. Med. Arom. Plants.*, **2011,** 1: 153-161
[41] Haroon K, Murad A K, Iqbal H. *J. Enz. Inhibit. Med. Chem.*, **2008,** 22: 722-725
[42] Srivastava U C, Chandra V. *J. Res. Indi. Med.*, **1977,** 10: 92-95
[43] Chitra R, Rajamani K. *Acad. J. Plant Sci.*, **2009,** 2: 39-43.
[44] Lalitha A, Ramesh S, Rajeswari S. *Electrochim. Acta.*, **2005,** 51: 47-55
[45] Kavithamani D, Umadevi M, Geetha S. *Indian J. Res. Pharm. Biotech.*, **2013,** 1: 554-558
[46] Li W, He Q, Zhang S, Pei C, Hou B J. *Appl. Electrochem.*, **2008,** 38: 289-295
[47] Selvarani F R, Santhanalakshmi S, Sahayaraj J W, John Amalraj A, Susai Rajendran S. *Bull. Electrochem.*, **2004,** 20: 561-565
[48] Susai Rajendran S, Mary Reenkala, Noreen Anthony, Ramaraj R. *Corr. Sci.*, **2002,** 44: 2243-2252
[49] Fawcett W R, Kovacova Z, Motheo A J, Foss C A. *J. Electroanal. Chem.*, **1992,** 326: 91-103
[50] Lebrini M, Robert F, Roos C. *Int. J. Electrochem. Sci.*, **2010,** 5: 1698-1712
[51] Saratha R. Vasudha V G. *E-J. Chem.*, **2010,** 7: 677-684
[52] Badiea A M, Mohana K N, *J. Mater Eng. Perfor.*, **2009,** 18: 1264-1271
[53] Raja PB, Rahim A A, Osman H, Awang K. *Physicochimica Sinica.*, **2010,** 26: 2171-2176
[54] Sarmila A, Prema AA, Sahayaraj PA. *Rasa. J. Chem.*, **2010,** 3: 74-81
[55] Velazquez-Gonzalez M A, Gonzalez-Rodriguez J G, Valladares-Cisneros M G, Hermoso-Diaz I A. Amer. *J. Anal. Chem.*, **2014,** 5: 55-64
[56] Ehteram Noor A. *J. Appl. Electrochem.*, **2009,** 39: 1465-1475
[57] Patel NS, Jauhariand S, Mehta GN, Al-Deyab SS, Warad I, Hammouti B. *Int. J. Electrochem. Sci.*, **2013,** 8: 2635-2655
[58] Rekha Nair N, Shashi Sharma, Sharma I K, Verma P S, Alka Sharma. *Rasa. J. Chem.*, **2010,** 3: 783-795
[59] Srikanth A P, Lavanya A, Nanjundan S, Rajendran N. *Appl. Sur. Sci.*, **2006,** 253: 1810-1816