IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 12, Issue 3 Ser. I (March. 2019), PP 77-82
www.iosrjournals.org

Corrosion Resistance of Mild Steel Using Harpulia Arborea Leaves As Green Inhibitor in HCL Medium

Judithaa.M.J[1], Jeevitha.R[2] and Srikanth.A.P[*]
PG & Research Department of Chemistry, Government Arts College (Autonomous), TN, INDIA
Corresponding Author: A.P. Srikanth,

Abstract: *The resistance to corrosion due to the presence of Harpulia Arborea leaves (HAL) extract on mild steel specimen in the presence of corrosive medium was examined by different kinds of techniques such as weight loss measurement, Immersion time, Electrochemical impedance spectroscopy, potentiodynamic polarization, Effect of temperature, Kinetics and Thermodynamic parameters and SEM morphology. The corrosion rate was decreasing with increase in concentration of the extract. The inhibition efficiency was increasing as the concentration of the extract was increased in the potentiodynamic polarization technique and the Tafel graph indicates that the HAL extract acted as a mixed type of inhibitor. Electrochemical impedance spectroscopy made known that the plant extract got adsorbed on the metal surface. The SEM morphology which was examined showed that the protective film was surrounded on the metal surface proved that HAL acted as a good corrosion inhibitor.*

Key words: *Corrosion inhibitor, EIS, SEM, polarization, kinetic parameters*.

Date of Submission: 11-03-2019 Date of acceptance: 27-03-2019

I. Introduction

In most industries where amenities were constituted by metallic structures, corrosion was habitually in attendance. This crisis developed very important material and economic fatalities of partly or total replacement of equipment and plant-repairing shutdowns. Corrosion affects the economic as well as social status, it means that the health of people either working in industries or living in nearby towns. The purpose of using corrosion inhibitors provided the most economical ways to alleviate the corrosion rate, shielding metal parts against corrosion and conserve industrial conveniences [1,2]. Economically and environmentally, plant extracts were an outstanding substitute as inhibitors due to their ease of use and biodegradability. In these supernatant liquids conjugated aromatic structures, long aliphatic chains such as nitrogen, sulfur, and oxygen hetero atoms with lone pair of electrons could proceed to put on view in superior efficiency on the subject of the decaying of the metal [3].

II. Materials And Methods

2.1 Preparation of Mild Steel Specimen:

Rectangular samples of area (2 x 5 x 0.2 cm) was being cut from a giant mass of mild steel. The specimens (mild steel coupons) were instinctively refined. These samples were the working electrodes [4]. The electrode cylindrically made and covered by Teflon tubes was the working electrode. The uncovered area of the metal surface was $1cm^2$. It was used for undergoing the studies such as electrochemical impedance spectroscopy and potentiodynamic polarization techniques [5].

2.2Preparation of the Plant Extract:

The *HAL* were collected, washed, dried for two weeks and powdered. Using reflux condenser, 25g of the powder was mixed with 500 mL of the double distilled water, kept in a water bath for 3 hrs and kept overnight. It was then filtered and the filtrate was made upto 500mL. Using this stock solution different concentrations were prepared.

III. Methods

3.1 Weight Loss Method:

The weight loss method was carried out by suspending the previously abraded mild steel specimens in HCl of 1N concentration in the absence and presence of the HAL extract. This process was prolonged for 24 hrs in the room temperature. The results were reported by accurately weighing the weight loss took place on the metal surface. From the reports, the corrosion rate and inhibition efficiency were calculated using the following relation.

$$CR\ (mmpy) = \frac{KXW}{DXAXT} \quad (1)$$

Where, $K = 8.76x10^4$, D = Density in gm/cm^3 (7.86), W = Weight loss in grams, A = Area in cm^2, T = Time in hrs.

$$IE\ (\%) = \frac{W_0 - W_i}{W_0} X\ 100 \quad (2)$$

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

3.2 FT-IR Analysis:

The various functional groups present in the HAL extract could be found out by FTIR spectra by using Bruker ALPHA 8400 spectrophotometer.

3.3 Scanning Electron Microscopy:

The surface morphological study of MS specimens dipped in the blank as well as the optimum concentration of the HAL extract was studied using MIRA3 TESCAN ultra high resolution field emission scanning electron microscope (FE-SEM) equipped with accessories for energy dispersive spectroscopy (EDS) analysis [6].

3.3 Effect of Temperature:

Inorder to know the effect of temperature on the inhibition efficiency and corrosion rate of mild steel strips which were suspended in 1N HCl solution containing the varied concentrations of plant extract with different temperatures ranging from 313K to 353K were conducted in 1 hour time duration [7].

3.4 Potentiodynamic Polarization Method:

Potentiodynamic polarization and AC impedance were brought about using CH instrument model 680 Amp Booster. It was composed of conventional three electrode cell. One of the three was the working electrode which was in the form of cylindrical shape devised from mild steel coated with Teflon. The other two electrodes were counter electrode which was a platinum foil and the reference electrode was a saturated calomel electrode were employed. The Tafel lines obtained from this study were extrapolated to calculate the corrosion current, corrosion potential. From those values the inhibition efficiency could be calculated [7].

The formula used to calculate inhibition efficiency is:

$$IE\% = \frac{Icorr\ (Blank) - Icorr\ (inh)}{Icorr\ (Blank)} x100 \quad (3)$$

Where $I_{corr(inh)}$ and $I_{corr(Blank)}$ are corrosion current in the presence and absence of inhibitor.

3.5 Electrochemical Impedence Method:

The impedance spectra were taken at room temperature in the frequency range of 1 HZ to 10,000 HZ. Before proceeding with the experiment a stabilization period of 15 minutes immersion was taken followed by recording open circuit potential [8]. A graph was plotted between the real part and imaginary part. The graphical values were used to find out the weight loss and the inhibition efficiency occurred. The inhibition efficiency in the absence and presence of the different inhibitor concentrations were calculated using the formula

$$IE\% = \frac{Rct\ (inh) - Rct\ (Blank)}{Rct\ (Blank)} x\ 100 \quad (4)$$

Where, $R_{ct\ (inh)}$ and $R_{ct\ (Blank)}$ are the charge transfer resistance in the presence and absence of the plant extract.

IV. Results And Discussion

4.1 Weight Loss Method:

As a result of exploration, the percentage of inhibition efficiency and corrosion rate were procured with the help of the equations (1) & (2) respectively [9,10,11]. The mild steel strips were plunged in non-identical concentrations of HAL extracts fluctuated or varied from 5 to 25ml in 1N HCl for 24 hrs. The outcomes are listed in Table-1. It was visible that the inhibition efficiency was increased from 5 to 25 mL. The most appropriate concentration was found to be 25 mL of IE% about 95.33%.

Table. 1 Weight Loss Determination of Mild Steel in 1N HCl Solution Containing Various Concentration of HAL Extract

Conc of HAL (ml)	CR (mmpy)	IE (%)
Blank	333.51	*
5	43.28	87.02
10	33.62	89.00
15	25.93	92.22
20	20.52	93.85
25	15.58	95.33

4.2 Effect of Immersion Time: The corrosion of mild steel in dissimilar concentration with miscellaneous immersion time in the presence and absence of inhibitor are recorded in Table-2. This was communicating that the dissolution of mild steel decreased with increase in concentration,furthermore increase in immersion time [12]. The extreme inhibition efficiency was endowed to be in the elevated concentration of 25 mL.

Table.2 Variation in Immersion Time

Conc in HAL (ml)	% of Inhibition efficiency						
	1h	3h	5h	7h	9h	12h	24h
5	65.55	70.88	77.94	80.02	86.50	89.44	90.94
10	66.01	76.94	83.35	84.73	90.48	91.73	93.01
15	69.00	79.43	85.09	86.38	92.19	92.69	93.47
20	70.50	83.91	87.88	90.05	93.98	95.75	95.11
25	73.15	86.79	90.22	93.41	95.38	96.46	96.46

4.3 FT-IR: From the Figure 1 it was evident that the HAL extract had definite functional groups. The band at 3325 cm^{-1}committed to O-H functional group. There was an existence of C-H stretching frequency which was confirmed by the presence of bands at 2923.75cm^{-1} [13]. The broad band at 1610.55cm^{-1} was attributed to C=O stretching frequency. The frequency range at 1380.31cm^{-1} which corresponded to C=C stretching vibration [14]. Two peaks were found at the ranges of 1158.06cm^{-1} and 1060.34cm^{-1} due to the presence of C-O and C-O-C stretching frequencies. The peak below 1000cm^{-1} corresponded to aliphatic C-H group [15]. There was the interaction of lone pair of electrons present in the hydroxyl group. The existence of oxygen atom and the unsaturated bonds of aromatic rings were the evidences
for the HAL extract acted as a corrosion inhibitor [16]

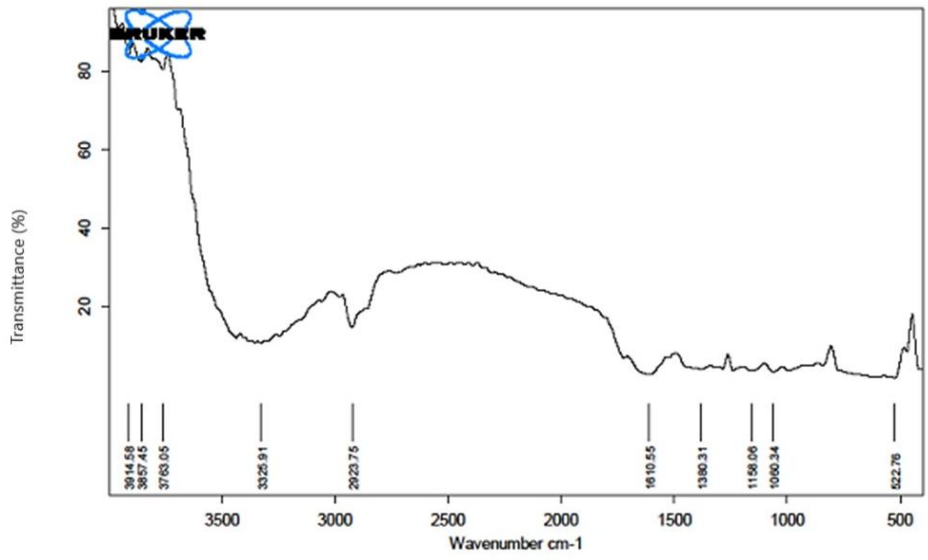


Figure 1. FTIR spectrum of *HA* Leaves extract

4.4 Potentiodynamic Polarizatiion Method: The cathodic and anodic polarization plots of mild steel drowned in 1N HCl in the existence and non-existence of different concentrations of plant extract were exhibited in Figure 2. The results were enlisted in the table 3. It could be recognized that corrosion potential values were increased and current density values were decreased for MS in the inhibitor–containing solution than inhibitor-free solution. The polarization curves proved that there was an hydrogen evolution on the cathodic slope and dissolution of metal on the anodic slope had been achieved. The process on the cathodic part was because of the formation of the barrier on the surface of the metal due to the inhibitor adsorption. The anodic dissolution was due to the presence of energy barrier created due to the inhibitor. There was no remarkable changes due to the presence of varied concentrations of the inhibitor implying that it is a mixed type of inhibitor which was causing both dissolution of metal and evolution of hydrogen [17]. The highest inhibition efficiency was found to be 94.29 % where the inhibitor volume is about 25 mL which was the optimum concentration.

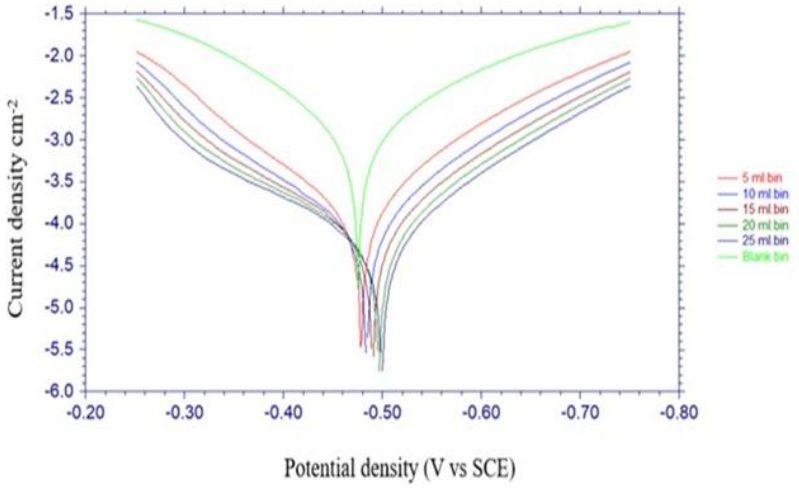


Figure 2. Tafel slope of Mild steel in the blank and HAL extract of different concentration.

Table.3 The Various Parameters of Potentiodynamic Polarization for Mild Steel in Various Concentrations of HAL Extract with 1N HCl

Conc of HAL (ml)	E_{corr} (mV)vs(SCE)	I_{corr} mA/cm^2	bc mV/dec	ba mV/dec	IE%
Blank	-0.4763	1.17	149.45	131.15	*
5	-0.4784	0.1307	98.92	120.18	88.83
10	-0.4841	0.09381	99.47	132.26	91.98
15	-0.4904	0.08327	109.77	152.28	92.88
20	-0.4963	0.07377	113.36	164.58	93.69
25	-0.4989	0.06685	118.37	179.44	94.29

4.5 Electrochemical Impedence Spectroscopy:

Electrochemical impedance spectroscopy was performed to study surface phenomena and electrode/electrolyte interface. In order to get the Nyquist plot, the corroding medium of 1N HCl with five different concentrations of the inhibitor along with the blank solution were used. It was examined that the region of the semicircle got enlarged with increase in concentration of inhibitor. Due to the adsorption of the inhibitor, the molecules present in the inhibitor produced the passive film that was spreaded over the metal surface which might cause corrosion resistance. The values are listed in the table 4. which displayed that there would be increase in R_{ct} value and decrease in C_{dl} value with increase in the concentration of the plant extract. There would be increase in the thickness of the electrical double layer, accustomed that the adsorption mechanism played a major role which formed a double layer interface.

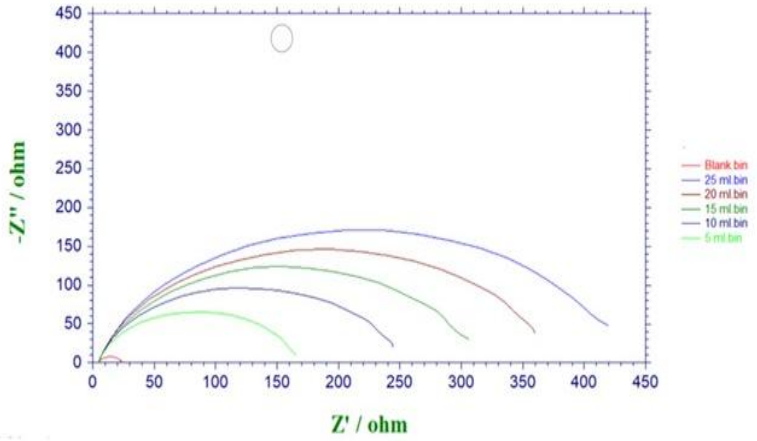


Figure 3. Nyquist plot of electrochemical impedance spectroscopy in the presence and absence of inhibitor

Table. 4 Measurement of Impedence for the MS with Various Concentrations of Plant Extract in 1N HCL.

Conc of HAL (ml)	C_{dl} (μFcm^{-2})	R_{ct} Ωcm^2	IE%
Blank	$4.99x10^{-5}$	17.65	*
5	$3.473x10^{-5}$	143.1	87.66
10	$3.099x10^{-5}$	210.1	91.60
15	$2.763x10^{-5}$	261.5	93.25
20	$2.575x10^{-5}$	308.6	94.28
25	$2.452x10^{-5}$	357.1	95.05

4.6 Impact of Temperature:

To compute the impact of temperature on deterioration and strengthening process, MS specimens were bared in the blank and in the existence of distinct concentrations of HAL extract at disparate temperatures ranging from 313K to 353K. The particulars are indexed in table 5. It was found that HAL extract impede mild steel in 1N HCl till 343K and downturn thereafter. The maximal value of inhibition efficiency was found to be 95.82% at 343K in 25 mL.

Table. 5 Inhibition Efficiency of HAL Extracts at Various Temperatures.

Conc of HAL(ml)	313K		323K		333K		343K		353K	
	CR	IE	CR	IE	CR	IE	CR	IE	CR	IE
Blank	805.23	*	1422.38	*	2118.95	*	2564.75	*	2727.75	*
5	199.81	85.12	168.57	88.14	190.85	90.99	208.97	91.85	477.84	82.48
10	103.09	87.20	86.37	93.93	121.20	94.28	110.06	95.71	288.37	89.43
15	91.95	88.58	78.01	94.51	91.94	95.66	107.27	95.82	214.54	92.13
20	87.77	89.10	72.44	94.91	89.16	95.79	105.88	95.87	189.46	93.05
25	84.98	89.45	68.26	95.20	76.62	96.38	94.73	96.31	176.93	93.51

4.7 Adsorption Isotherm:

Adsorption isotherm plays indispensable role in resolving the mechanism of organo-electrochemical reactions. The intermittently used isotherms are Langmuir, Frumkin, Parsons, Temkin. A plot was drawn between C/θ vs C for mild steel in acidic environment in presence of various concentration of the extract. A straight line was obtained which demonstrated that the adsorption of the HAL extract on MS obeyed Langmuir adsorption isotherm [18].

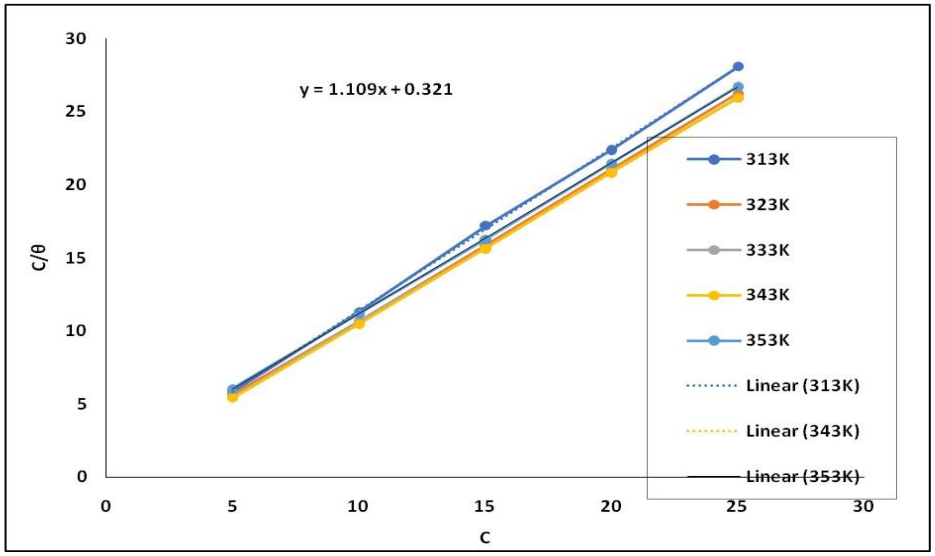
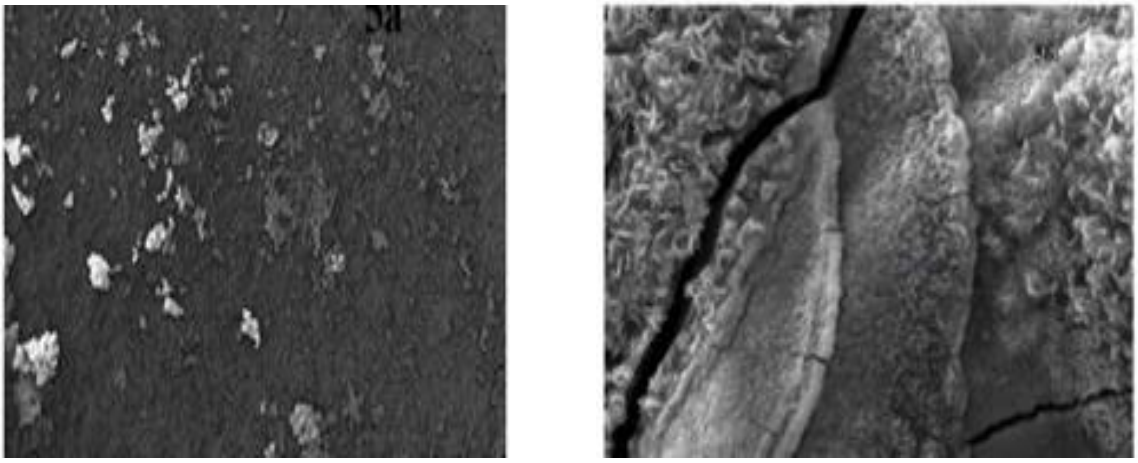


Figure 4. Langumuir adsorption isotherm plot for mild steel in 1N HCl with Harpulia Arborea leaves extract

4.8 Scanning Electron Microscopy (SEM):

By using scanning electron microscopy the surface analysis of mild steel dipped in blank and with the optimal concentration of the plant extract were analyzed for 24 hrs. In Figure (5a) it was clearly shown that the mild steel surface in blank solution was badly corroded due to the corrosiveness of acid. In Figure (5b) it was concluded that the metal surface was protected from deterioration due to the adsorption of plant inhibitor [19].



(5a) (5b)

Figure 5. SEM morphology of mild steel in the absence of inhibitor (5a) and in the presence of inhibitor (5b)

V. Conclusion

It was concluded that the HAL acted as a good green corrosion inhibitor in aggressive acid medium which showed that the inhibition efficiency was found to be about 95.33% at optimum concentration. The adsorption study revealed that the plant inhibitor obeyed chemisorption till 343K thereby followed physisorption as the inhibition efficiency decreased due to the rise in temperature. In polarization techniques at cathode, there was the formation of the barrier on the surface of the metal due to the inhibitor adsorption. The anodic dissolution took place because of the energy barrier created due to the inhibitor. There was no remarkable changes due to the presence of varied concentrations of the inhibitor implying that it was a mixed type of inhibitor. The protective film was formed due to the adsorption of inhibitor on the surface of the metal was obvious from the SEM morphology.

References

[1]. Sastri VS, Green Corrosion Inhibitors. Theory and Practice. John Wiley & Sons:Hoboken, NJ; 1998.
[2]. Sastri VS. Corrosion Inhibitors Principles and Applications. John Wiley & Sons: NewYork; 1998.
[3]. Rafael Martinez Palou, Octavio Olivares-Xomeltand Natalya V. Likhanova,"Environmentally Friendly Corrosion inhibitors".
[4]. Saratha and V.G.Vasudha, E-J.Chem,7, 3,(2010).
[5]. J. Buchweishaija, G. S. Mhinzi, *Port Electrochim Acta* 26, (2008).
[6]. K.K.Alaneme,S.J. Olusegan and A.W.Alo,Alex. Eng. J, 55, (2016).
[7]. R.S. Nathiya, Vairamuthu Raj, Egypt.j.Petrol 26, (2017).
[8]. NamrataChaubey, Vinod Kumar Singh and M.A. Quraishi, Ain Shams Eng. J, 9, (2018).
[9]. L. R. Chaulhan and G. Gunasekaran, Corros Sci, 49, 3, (2007). doi:10.1016/j.corsci.2006.08.012
[10]. E. E. Oguzie, Mater Chem and Phys, 99, 2-3, (2006). doi:10.1016/j.electacta.2004.04.030
[11]. E. Chaieb, A. Bouyanzer, B. Hammouti and M. Berrabh, ACTA PHYS -CHIM SIN, 25, 7, (2009).
[12]. E.N. Dim, P.O. Ukoha and N.L. Obasi, ASIAN J CHEM, 24, 5, (2012).
[13]. K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, Corros. Sci. 51, (2009).
[14]. M.Karuppusamy, P. R. Sivakumar,S. Perumal,A. Elangovan, A. P. Srikanth, J. Environ Nanotechnol, 2 (2015).
[15]. M.Ramanandasingh, Prachi Gupta, Kaushal Gupta, *ARAB J CHEM*, 2015.
[16]. S. Firdausi and F. Kurniawan, J. Phys. Conf. Ser, 710 (2016).
[17]. Gopiraman, Mayakrishnan, ·SakunthalaPitchai, Kanmani Raman, Alex Ramani Vincent, SulochanaNagarajan, Researchgate, Ionics 17, (2011).
[18]. P. Premkumar, K. Kannan and M. Natesan, ASIAN J CHEM, 20, 1, (2008).
[19]. E.E.Ebenso, N.O.Eddy and O.A. Odiongenyi, Afr. J. Pure. Appl. Chem, 107, (2008).

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

A.P. Srikanth,. "Corrosion Resistance of Mild Steel Using Harpulia Arborea Leaves As Green Inhibitor in HCL Medium." IOSR Journal of Applied Chemistry (IOSR-JAC) 12.3 (2019): 77-82.