Enhanced corrosion resistance of mild steel in hydrochloric acid solution by sida acuta bunn.f leaf extract: electrochemical study.

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Abstract- **The biodegradable inhibitor, which could effectively reduce the rate of corrosion of mild steel, were investigated by chemical (weight loss) & Electrochemical (potentiodynamic polarization & Electrochemical Impedance Spectroscopy (EIS)) techniques. The mixed type inhibitors extracted from sida acuta leaf exhibited excellent inhibition performance, & the inhibition efficiency for mild steel reached 97.60% at 298 K in hydrochloric acid. Moreover, the adsorption mechanism of the inhibitors on a mild steel surface is described by the Langmuir adsorption isotherm. The morphology of the surface of the specimens was analysed using atomic force microscopy, energy dispersion spectroscopy & scanning electron microscopy. The results obtained from chemical & electrochemical techniques are in good agreement.**

key words: sida acuta leaf, inhibition efficiency, EIS, SEM, AFM,

I. INTRODUCTION

The study of mild steel corrosion is theoretical and practical importance. Acid solutions are widely used for the removal of rust and scale in several industrial processes such as pickling, chemical and electrochemical etching, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid decaling, resulting in huge economic losses and many potential safety questions due to metallic corrosion [1]. Corrosion inhibitor of organic matter is preferred because it has relatively high affinity to the metal, its value of high efficiency, and also eco-friendly. The effectiveness of organic compounds as inhibitor has been greatly influenced by the presence of hetero atoms (O,N,P and S), polar groups, pi-bond, and the lone pair as it becomes a mean for inhibitors to do coordinated chemisorptions binding to the metal [2,3]. There has been extensive research done to develop inhibitors that are cost effective and environmentally friendly. Most of the inhibitors developed from natural sources such as plants are found to have the presence of heterocyclic compounds, nitrogen, sulfur and oxygen atoms and these contribute greatly to inhibit ion of corrosion via various mechanisms. Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [4].

Sida acuta Bunn.f. (Sida acuta) (Family of Malvaceae) is an erect perennial shrub found throughout the hotter parts of India and Nepal [5]. In Indian traditional medicine, the root of sida acuta is extensively used as a stomachic, diaphoretic and antipyretic [6]. It is regarded as cooling, astringent, tonic and useful in treating nervous and urinary diseases and also disorders of the blood, bile and liver [7]. The whole plant is used to treat snake bite. sida acuta has significant antiplasmodial activity due to its alkaloid content [8]. The paste of leaves is mixed with coconut oil and applied on head regularly for killing dandruffs and also for strengthening hair. It is naturally used in the treatment of malaria, diarrhea and many other diseases [9]. However, the leaves have never been exploited as the corrosion inhibitor in acid medium. Hence, the goal of the present paper is to test the extract of Sida acuta leaf as an environmentally friendly inhibitor for the acid corrosion of mild steel, by various techniques such as weight loss and electrochemical measurements.

II. MATERIALS AND METHODS

2.1. Preparation of mild steel specimen

Mild steel strips were mechanically cut into strips of size 4cm x 2cm x 0.1cm containing the composition of (C-0.030%, Mn-0.169%, Si-0.015%, P-0.031%, S-0.029%, Ni-0.030%, Mb-0.016% and Cu-0.017%) and remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of $1cm^2$ were used. Mild steel strips were polished by using emery paper of (400, 600, 800, 1000 and 1200) grade, it was then dried and stored in desicator to avoid moisture before using it for corrosion studies.

2.2. Preparation of Plant Extract

The Sida acuta plant leaves were taken and cut into small pieces, and dried in room temperature and ground well into powder. 20g of the powder was refluxed in 200ml ethanol and it was kept overnight. The refluxed solution was filtered and the filtered liquor was evaporated to dark green residue

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and extracted with separating funnel. The solution was evaporated and the dark green solid residue obtained after complete drying was preserved in a desicator. The residue so obtained was used in preparing different concentrations of the extracts in hydrochloric acid solution. The solution was expressed in v/v.

2.3. Weight loss method

In mass loss measurements, specimen of mild steel is immersed exactly in 100ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after 60 minutes to 180 minutes at room temperature. From this mass loss, the corrosion rate (mmpy-millimetre per year), percentage inhibition efficiency was calculated using the formula,

Corrosion rate (mmpy) = Weight loss×87.6/ (Area×Time×Metal density)

Where mass loss is expressed in gm, area is expressed in cm^2 of metal surface exposed, time is expressed in minutes of exposure, and metal density is expressed in $gm/cm^3$and 87.6 is conversion factor. Inhibition efficiency was calculated as

$IE\% = 100 ((W_o-W_i) /W_o)$,

The degree of surface coverage (θ) can be calculated as

$\theta = (W_o-Wi) /W_o$

Where θ surface coverage and Wo and Wi are the mass loss of the metal in uninhibited and inhibited basic solution [10, 11]. Accuracy in weighing up to 0.0001g and in surface area 1cm2, as recommended by Denver balance TP 214 model.

2.4 Phytochemical screening

Phytochemical screening was carried out on the freshly prepared ethanol extract of S. Acuta leaf as per standard procedures [12].

2.5 Electrochemical and impedance measurements

A three- electrode cell, consisting of a mild steel rod working electrode (WE), a platinum counter electrode (CE), and saturated calomel electrode (SCE) was used for measurements. The electrolyte used was acidic solution maintained at 250 C. Electrochemical impedance measurements through Nyquist plot and polarization studies through Tafel plot have been carried out using CH Elecrochemical analyser model 650 C (USA).

2.6 Morphology Analysis

The mild steel specimen immersed in blank and in the inhibitor solution for a period of 3 hours was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of mild steel were examined using (JOEL) computer controlled scanning electron microscope. An EDS detector is used to separate the characteristic X-rays of different elements into an energy spectrum and EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The protective film was carefully removed, mixed thoroughly with KBr and made in to pellets and FTIR spectra were recorded.

2.7 Atomic Force Microscopy (AFM)

AFM is the most versatile and powerful microscopy whereby the sample surface was scanned by a fine tip to find out the surface morphology and properties to generate a3D surface image. The surface morphology was calculated using an SPM 2100 AFM instrument operating in contact mode in air; the scan rate of all AFM images was 05µm× 05µm areas at a scan speed of 6.68 µm second.

III. RESULTS AND DISCUSSION

3.1. Determination of corrosion rates and inhibition efficiency:

The corrosion rate of mild steel in solutions containing 1M HCl in the absence and presence of various concentrations of inhibitor obtained by the weight – loss method for 60 minutes, 120 minutes, and 180 minutes are given in Table 1.

TABLE1. Data from Weight Loss Method for Mild Steel corrosion in 1M HCL solutions at various concentrations of S.acuta leaf extract

Conc. of S. acuta leaf extract (v/v)	60 minutes		120 minutes		180 minutes	
	I.E	CR	I.E	CR	I.E	CR
Blank	0	0.0161	0	0.0458	0	0.06753
5	71.9	0.0042	95.1	0.0033	89.4	0.0048
10	83.1	0.0027	96.1	0.0026	90.5	0.0039
15	82.7	0.0024	96.6	0.0023	91.6	0.0034
20	86.0	0.0021	97.6	0.0016	92.8	0.0031
25	85.5	0.0028	95.8	0.0030	91.1	0.0037

It is observed from the table that the corrosion rate decreased and thus inhibition efficiency increases with increasing concentration of S.acuta extract (5v/v – 25v/v). The maximum inhibition efficiency of about 97.6 % was achieved at 20v/v of S.acuta extract. This behaviour is due to the fact the adsorption and coverage of the inhibitor on the mild steel surface interaction with the inhibitor concentration [13]. This result indicated that S.acuta extract could act as an excellent corrosion inhibitor. At concentration ≥ 25 v/v of S.acuta extract the protection efficiency decreases. It may be due to the fact that extracts molecules aggregate together to form micelles. They are not uniformly adsorbed on the metal surface. Hence corrosion inhibition efficiency decreases.

3.2 Adsorbtion consideration

The plots of C/Θ against C (v/v) that is linear (Figure 1) shows that S. Acuta extract obeys the Langmuir isotherm at the concentration and room temperature studied for the metal.

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The plots support the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a protective film on the metal surface and that the additive covers both the anodic and cathodic sites through uniform adsorption following Langmuir isotherm.

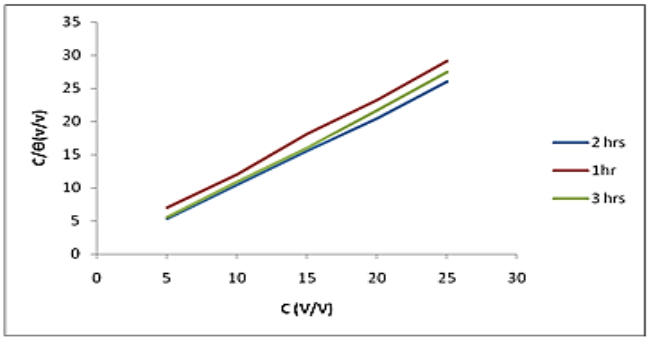

Figure1. Langmuir adsorption isotherms plotted as C/Θ versus C for inhibition of mild steel corrosion in 1M HCL solution by S. Acuta extract

3.3 Phytochemical screening method

Phytochemical analysis of S. Acuta leaf extract was tested in order to find the presence of various chemical constituents included alkaloids, carbohydrates, proteins, saponins, triterpinoids and tannins are listed in Table 2

Table 2. Preliminary phytochemical analysis of S. Acuta leaf extract

S.No	Phytochemical test	Alcoholic extract of *S. Acuta*
1.	Alkaloids	+
2	Carbohydrates	+
3	Proteins	+
4	Glycosides	+
5	Flavonoids	+
6	Tannins	–
7	Phenolic compounds	+

3.4 FTIR measurement

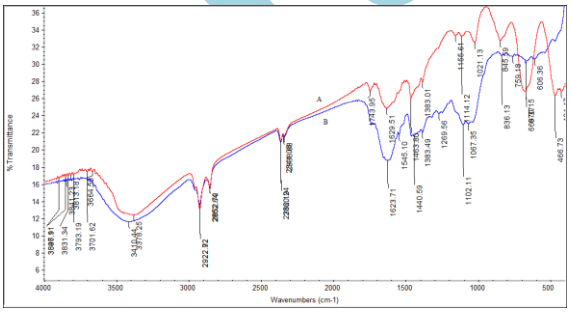

Figure 2. FTIR spectra of the (A) film created on the mild steel immersed in IM HCL and (B) S. Acuta extract

Earlier researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the the type of bonding for organic inhibitors adsorbed on the metal surface [14]. Figuer 2 (A and B) represent the IR spectrum of film created on the mild steel immersed in 1M HCL and *S. Acuta* leaf extract.The components present in the extract form protective film on the metal surface by coordinating with the metal ion through O, S and N atoms of the functional groups present in the components [15]. C=O stretch is present at 1623 cm^{-1}. This is shifted to 1629 cm^{-1} indicating the coordination of carbonyl group to the surface of the steel. The presence of new band at 467 cm^{-1} may be due to the Fe-O stretch. The –N-H stretch is present at 3410 cm^{-1} [16] and this disappears in the corrosion product showing the coordination of nitrogen. There is more number of new bands are shifted to different frequencies indicating the coordination of groups to the metals in steel. The corrosion products contain extracts. Therefore from the spectra it is revealed that the inhibition is due to the adsorption of corresponding organic molecule.

3.5 Potentiodynamic polarization studies

The potentiodynamic polarization data are shown as the Tafel plots for mild steel in 1M HCL with the addition of various concentrations of the additive in Figure 2. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and anodic and catodic Tafel slopes (b_a and b_c), were derived from these curves and are given in Table 2.The values of E_I % are calculated using the following equation:

$$IE(\%) = ((I_{corr} - I^*_{corr}) / I_{corr})100$$

Where I_{corr} and I^*_{corr} are the values of corrosion current densities of mild steel without and with the additive, respectively,which were determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential $E_{corr.}$ From the Table 2, it is observed that the I_{corr} values are progressively decreased with gradual increases in the concentration of additives. The maximum inhibition efficiency of 82% was obtained at 20v/v, was considered as the optimum concentration of the inhibitor.

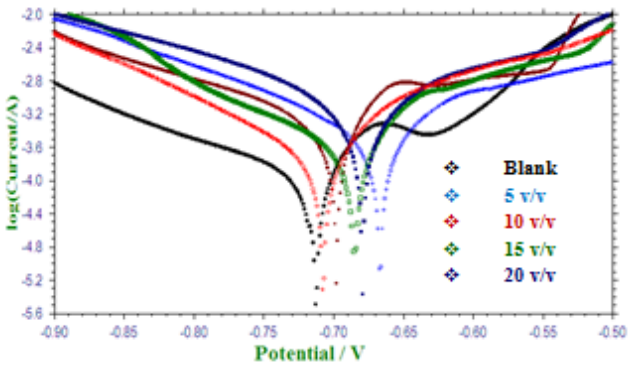

Figure 3. Tafel plots showing effect of S.acuta leaf extracts on corrosion of mild steel in 1M HCL medium

Polarization study has been used to detect the formation of protective film on the metal surface. When compared with the blank 1M HCL, the S.acuta leaf extract showed a mixed mode of inhibition. Moreover in the presence of inhibition system, the corrosion current decreased from 8.433 to 1.501mAcm^{-2}. These observations confirmed the decrease in the oxidation of the metal and the formation of protective film on the metal surface [17].

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Table 3. Effect of S.acuta leaf extracts on mild steel in 1M HCL media at 250C (Tafel Polarization Studies)

Concentration of inhibitor (v/v)	E_{corr}(V)	Tafel constant (mV decade^{-1})		Corrsion Current Density I_{corr} (mA cm^{-2})	Inhibition Efficiency (%)
		b_a	b_c		
0	-0.713	204	228	8.433	-
5	-0.706	201	214	3.326	61
10	-0.698	199	228	3.012	64
15	-0.685	182	228	2.101	75
20	-.0.679	171	225	1.501	82
25	-0.665	166	224	1.524	81

3.6 Electrochemical Impedance Spectroscopy (EIS) Studies

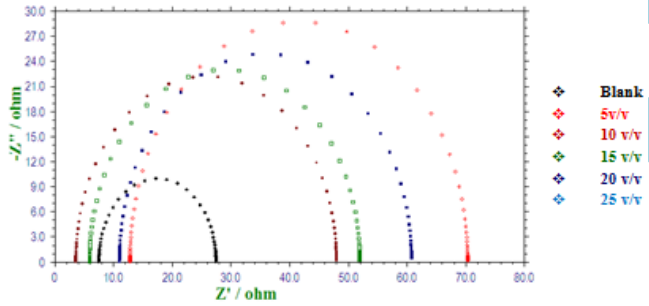

Figure 4. Nyquist plots for mild steel in 1M HCL acid solution without and with various concentration of S.acuta leaf extract

The corrosion behaviour of mild steel in 1M HCL in absence and presence of S.acuta leaf extract were investigated by EIS. Nyquist plots for mild steel in uninhibited and inhibited acid solutions containing different concentrations of S.acuta leaf extract are shown in Figure 4 and data are given in Table 4.The impedance spectra showed a single semicircle and as the concentration of inhibitor increases, diameter of the semicircle increases. It is evident from the results that S.acuta leaf extract inhibited the corrosion of mild steel in 1M HCL at all the concentrations used, and the inhibition efficiency increased continuously with increasing concentration.

The AC impedance of the inhibited system amplified with the inhibitor, the C_{dl} values decreased with inhibitor. This decrease in C_{dl} results from a decrease in local dielectric constant and /or an increase in thickness of the double layer suggested that inhibitor molecules inhibit the mild steel corrosion at the metal/acid interface [18]. The depression in Nyquist semicircles is a feature for mild steel electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogeneties of the mild steel [19].The increase in R_{ct} values is attributed to the formation of protective film at the metal solution interface [20, 21].These observations suggest that *S.acuta* leaf extract function by adsorption at the metal surface thereby causing decrease in C_{dl} values and increase in R_{ct} values. `

The values of inhibition efficiency IE % were calculated by the following as follows:

$$IE\% = ((R_{ct} - R^0_{ct}) / R_{ct})\ 100$$

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

To obtain the values of $C_{dl,}$ the values of frequency (f_{max}) at which the imaginary component of the impedance is maximum $-Z_{in(max)}$ was found and used in the following equation with corresponding R_{ct} values.

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

Table 4.Electrochemical impedance parameters for mild steel in 1M HCL acid solution in the absence and presence of various concentration of inhibitor.

Concentration of *S.acuta* leaf extract	R_{ct} Ohm cm^2	C_{dl} µF cm^{-2}	Inhibition efficiency I.E. (%)
0	2.071	146.51	
5	4.552	73.27	56
10	7.176	63.08	71
15	10.423	53.73	80
20	14.097	44.97	85
25	14.182	35.73	85

3.7 Scanning electron microscopy(SEM) analysis

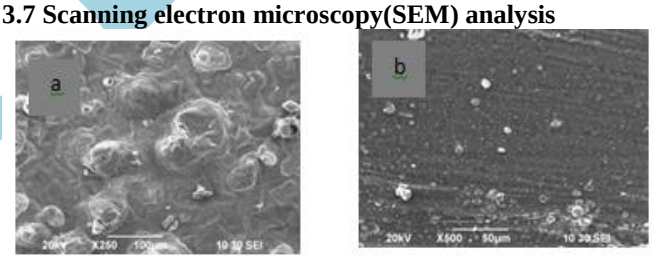

Figure 5. SEM images of (a) Polished mild steel coupon without inhibitor and (b) mild steel coupon with inhibitor

The surface morphology of the mild steel in 1M HCL in the absence and in presence of S. Acuta leaf extract are shown in Fig 4. The image (5a) shows badly damaged surface obtained when the metal was kept immersed in 1M HCL for 3 hours without inhibitor indicates significant corrosion. However, in the presence of inhibitor (Figure 5b), the surface has remarkedly improved with respect to its due to the formation of a good protective film of S. Acuta leaf extract on mild steel surface which is responsible for inhibition for corrosion[22].

3.8 EDAX Analysis

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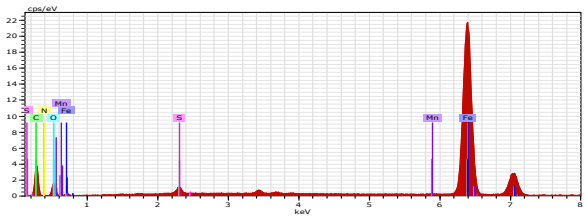

Figure 6. EDAX spectra for corrosion product on metal surface in the presence of inhibitor.

Root-mean- square roughness, average roughness and peak-to-valley value AFM image analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square –roughness, R_q (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak- to-valley (P-V) height values (largest single peak –to-valley height in five adjoining sampling heights) [26].Table 5 is a summary of (R_q) , (R_a), (P-V) value for mild steel surface immersed in different environment. Figure 2(a,d) displays the surface topography of un-corroded metal surface. The value of R_q, R_a, and P-V height for the polished metal steel surface (reference sample) are 17.948nm, 14.405nm and 36.542nm respectively.The slight roughness observed on the polished mild steel surface is due to atmospheric corrosion. Figure 2(b,e) displays the corroded metal surface with few fits in the absence of the inhibitor immersed in acid solution. The (R_q), (R_a), and (P-V) height values for the mild steel surface are 113.72nm, 88.033nm and 574.23nm respectively. These data suggests that mild steel surface immersed in acid solution has a greater roughness than the polished metal surface, which shows that the unprotected mild steel surface is rougher and was due to the corrosion of the mild steel in an acid environment. Figure 2(c, f) displays the steel surface after immersion in acid solution containing 20v/v of *S. Acuta* extract. The (R_q), (R_a), and (P-V) height values for the mild steel surface are 19.869nm, 13.66nm and 91.841nm respectively. The (R_q), (R_a), and (P-V) height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The decrease in the roughness value reflected the adsorption of extract molecules on metal surface thereby reducing the rate of corrosion.

Table 5. AFM data for mild steel surface immersed in inhibited and uninhibited environment

Samples	RMS(R_q) Roughness (nm)	Average (R_a) Roughness (nm)	Maximum Peak-to-valley Height (nm)
1.Polished mild steel	17.948	14.405	36.542
2.Mild steel immersed in acid solution(blank)	113.72	88.033	574.23
3. Mild steel immersed in acid solution containing *S.acuta* leaf extract(20v/v)	19.869	13.66	91.841

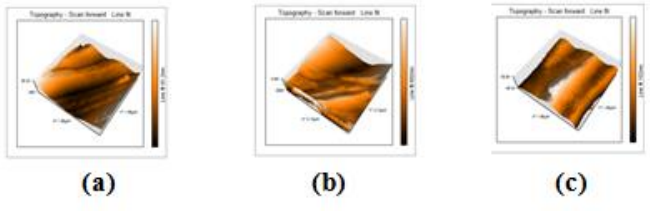

Figure 7. Three dimensional AFM images of the surface of a) As polished mild steel (control); b) mild steel immersed in acid solution (blank); c) mild Steel immersed in acid solution containing 20 v/v of Sida acuta extract

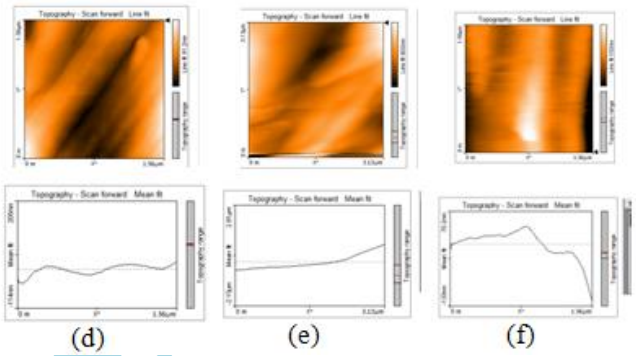

Figure 7. AFM Cross-sectional images of the surface of d) As polished mild steel (control); e) mild steel immersed in acid solution (blank); f) mild Steel immersed in acid solution containing 20 v/v of Sida acuta extract

IV. CONCLUSION

Sida acuta leaf acts as efficient corrosion pickling inhibitor on mild steel in 1M HCL acid. The use of S. Acuta plant as corrosion inhibitor is environmentally safe, nontoxic, and eco-friendly, cost effective and easily available. The Sida acuta leaf extracts showed maximum inhibition efficiency of 97.6% at the optimum concentration of 20v/v for 120 minutes immersion time at room temperature. Results obtained in non-electrochemical methods (weight-loss method) have good agreenment with the electrochemical methods.The S.auta leaf extracts acts as a mixed type inhibitor on the metal surface.Photographs by SEM have clearly shown the formation of protective film on the surface of mild steel.AFM studies confirm that the surface is smoother. The smoothness of the surface is due to the adsorption of extract molecules on metal surface thereby inhibiting the corrosion of mild steel. The results of the the electrochemical tests and weight loss measurements are consistent and show that this green inhibitor, which was isolated from the ethanol extract of Sida acuta leaf, can be potentially applied as an anticorrosive agent for mild steel in hydrochloric acid environment.

V.ACKNOWLEDGEMENT

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The present work was part of the project funded by University Grants commission [F.MRP-5712/15 (UGC-SERO)], Hyderabad. The first author wishes to thank the UGC and acknowledge its financial assistance with deepest gratitude.

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