Investigating the extract constituents and corrosion inhibiting ability of *Sida acuta* leaves

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ABSTRACT

Constituents of the ethanol extract of *Sida acuta* (SA) leaves were investigated by phytochemical, GC-MS and FTIR studies and its corrosion inhibition effects on mild steel was studied in 1 M HCl and 0.5 M H_2SO_4 solutions, using gravimetric and electrochemical methods of corrosion monitoring. The surface morphology of the mild steel surface before and after corrosion was also assessed using SEM imaging. The phytochemical, GC-MS and FTIR results revealed that SA contains carbonyl groups, aromatic rings, and double bonds that make it a prospective corrosion inhibitor for mild steel. Moreover, gravimetric results indicated that SA is an effective additive for the corrosion of mild steel at all the concentrations studied. Finally, the electrochemical results showed that SA inhibited both the anodic and cathodic half reactions by the adsorption of the extract constituents on the mild steel surface; this was further confirmed by the SEM investigations.

Keywords: *Sida acuta*, chemical constituents, mild steel, corrosion, inhibitor

1. INTRODUCTION

Mild steel finds application in many industries where acids are used. Therefore there is need to protect it from corrosion attack [1-5]. Corrosion is one of the major industrial problems known [6-10]. The best way to reduce metal corrosion is by using some additives which are harmless to human health. Many plant materials have been tried for their corrosion

inhibiting abilities and they have proven useful [11-13]. The corrosion inhibiting abilities of plant extracts may be attributed to their chemical constituents. It has been shown that plant materials containing elements such as sulphur, nitrogen and oxygen show good corrosion inhibiting properties [14-16].

These materials are biodegradable, inexpensive, readily available and ecologically friendly. These plant materials were hitherto used for food, clothing, shelter, medicine, fragrance etc., but due to the pressing need for non-toxic corrosion inhibitors, their use has been extended to material protection [17-25]. The present study investigates the active materials present in ethanol extract of *Sida acuta* leaves using GC-MS and FTIR analysis, and also tests the corrosion inhibiting ability of the plant material via gravimetric analysis and electrochemical methods of corrosion monitoring.

Photo 1. *Sida acuta*

2. EXPERIMENTAL/RESULTS

2. 1. Metal preparation

The metal used for the experiments was mild steel of the percentage composition C – 0.05; Mn – 0.6; P - 0.36; Si – 0.3 and the balance Fe. The mild steel specimens were prepared as described in our previous works [26-30, 42-46].

2. 2. Preparation of the plant material

The plant material used was *Sida acuta* (SA). Fresh leaves of SA were collected randomly around Imo state university environment, dried to low moisture content and grinded to a powdered form. 20g of the powdered SA leaves was percolated with 1000 ml of redistilled ethanol (98% ethanol) for a period of 24 hours. The sample was filtered with a filter cloth. The filtrate was used for the experiments while the residue was used to quantify the stock solution by subtracting the weight of the dried residue from the weight of the dried plant before it was extracted.

2. 3. Reagents used

The corrodents used were 1 M HCl and 0.5 M H_2SO_4 solutions. Distilled water was used for all material preparations and absolute ethanol was used for the extraction process.

2. 4. Quantitative phytochemical screening of plant material

Phytochemical screening involved carrying out simple analysis to determine the chemical constituents of SA. 2 g of the powdered sample was defatted with 100 ml of diethyl ether using a soxhlet apparatus for 2 h. Quantitative amounts of Alkaloids, Flavonoids, Saponins, Phenols and tannins in a the SA extract were then determined using standard laboratory procedures [31-33].

2. 5. Gas chromatography – mass spectroscopy analysis

The gas chromatography-mass spectroscopy analysis was done with SHIMADZU, JAPAN GCMS-QP2010 PLUS. The GC-MS analysis was undertaken to detect the organic compounds present in the SA extract. The experimental conditions were as follows; For GC-2010 conditions, the column oven temperature of 45 °C was used, the injection temperature was 250 °C, carrier gas was nitrogen, the carrier gas pressure was 94.3 KPa, the purge flow split was 3.00 mL/min with a ratio of 10.0, total flow rate was set as 21.0 mL/min and column flow rate of 1.64 mL/min. The oven temperature program was from 45-280 °C held at 45 °C for 2 min and raised to 280 °C for 3 min at the rate of 15 mL/min. The MS analysis was as follows the start time was 3.50 min and an end time of 27.00 min, the scan speed was 1250 with m/z range 18-600. Each chemical constituent of SA extract was compared with NIST05s LIB by matching with the mass spec. of published data [34].

2. 6. Gravimetric analysis

The mild steel coupons used for the gravimetric experiment was of the dimension 3 × 3 × 0.14 cm, The coupons were polished while wet with silicon carbide abrasive paper (from grade #400 to #1000) [35], they were rinsed in distilled water, dried using acetone and warm air, weighed and kept for use when needed. The gravimetric vessels were prepared by suspending the weighed coupons with twine under total immersion into 300mL of the test solutions at 30 °C. The systems were left unstirred and in aerated environments. To calculate the weight loss after each day, the text coupons were retrieved daily for 5 consecutive days. When retrieved, the coupons were immersed in a solution containing 20% NaOH and 200g/L of zinc dust [35] to momentarily stop the corrosion reaction, scrubbed with bristle brush, washed with distilled water, re-weighed and re-immersed into the test solution [36].

The weight loss was calculated by subtracting the weight of the coupon after each day from its initial weight before immersion.

2. 7. Electrochemical experiments

Mild steel coupons of dimension 1×1 cm^2 were used for the electrochemical experiments. These coupons were fixed in polytetrafluoroethylene (PTFE) rods using epoxy resins [37]. When fixed, only one side of the coupons of area 1 cm^2 where left uncovered. The area left uncovered was cleaned as in the gravimetric experiments. A conventional three electrode glass cell of capacity 400 mL was used for the electrochemical experiments using a VERSASTAT 400 complete DC Voltammetry and corrosion system with a V3 software [37]. The working electrode was the mild steel coupon; a graphite rod was used as the counter electrode while a saturated calomel electrode was used as the reference electrode. A luggin's capillary was used to connect the reference electrode; the system was left in an aerated and unstirred condition for 1 h at 30 °C. Electrochemical impedance spectroscopy experiments were carried out at corrosion potentials (E$_{corr}$) over a frequency range of 100 KHz -10 MHz at a signal amplitude perturbation of 5 mV [38]. Potentiodynamic polarization experiments were done in the potential range of ±250 mV versus corrosion potential at a scan rate of 0.333 Mv/s.

2. 8. Fourier transform infrared spectroscopy experiments

FTIR experiments were carried out to ascertain the functional groups present in the SA extract. An FTIR (KBr) Nicolet Magna-IR 560 spectrophotometer was used for the recording. The spectra of SA powder was taken by mixing it with KBr, and making the pellet for the FTIR examination [39].

2. 9. Scanning electron microscopy examination

Morphological study of the mild steel surfaces before and after immersion in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions were understudied using SHIMADZU SSX-550 scanning electron microscope. The mild steel specimens used for the SEM examination has the dimensions $15 \times 10 \times 2$ mm they were cleaned as described previously and immersed for 3 h in the corrodent solutions (1 M HCl and 0.5 M H$_2$SO$_4$) without and with 1000 mg/L SA at 30 ± 1 °C, and then cleaned with distilled water, dried with acetone, and subjected to SEM examination [40].

2. 10. Phytochemical results

Phytochemical analysis was performed to determine the chemical constituents of SA. The result of the phytochemical screening is presented in Table 1. The phytochemical result showed that SA contained high percentage of saponins some of which contains O, H and N in their structures. The presence of these phytochemicals in SA makes it a prospective material for corrosion inhibition. The GC-MS results showed the presence of 25 compounds (Figure 1), some of these compounds which contain some ingredient that have been reported to be active against metal corrosion are toluene, cyclohexane, n-Hexadenoic acid, 1,3-Decosenoic acid, 2-Hexadecen-1-ol and 1-Decanol as presented in Table 2. The presence of O, N, S and aromatic rings in these compounds confirms the susceptibility of SA as a good candidate for corrosion inhibition as already reported by other authors [41]
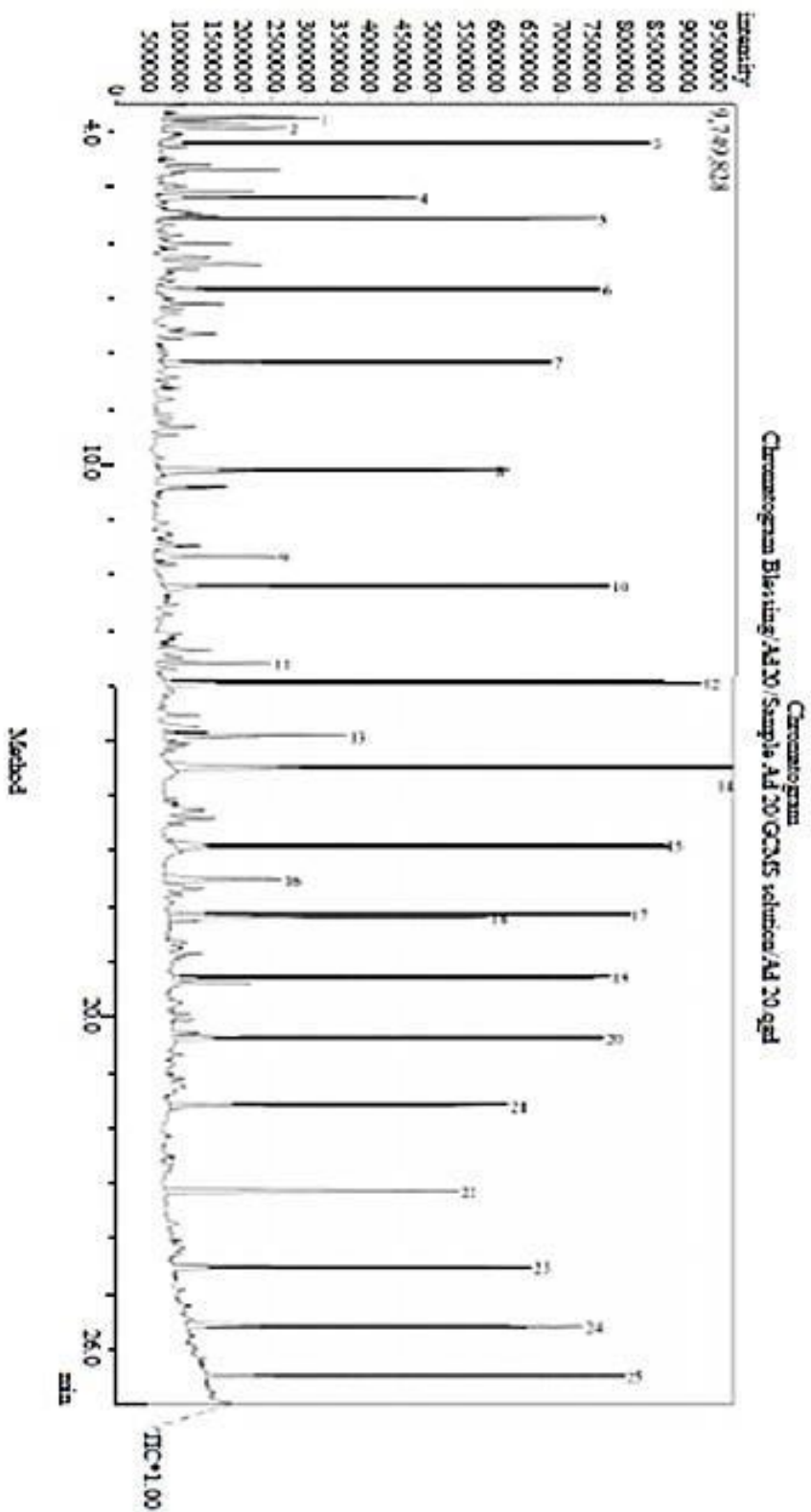
Figure 1. GC-MS Chromatogram of SA showing 25 peaks

Table 1. Result of quantitative phytochemical analysis.

PHYTOCHEMICAL	% ABUNDANCE
Flavonoids	0.038
Alkaloids	3.392
Saponins	21.95
Phenols	1.91 ppm
Tannins	8.36 ppm

Table 2. Result of GC-MS analysis

RETENTION TIME	NAME OF COMPOUND	MOLECULAR WEIGHT	AREA (%)
3.773	Toluene	92	1.51
3.936	Cyclohexane	112	1.50
5.198	Cyclopentane	112	2.40
19.270	n-Hexadecanoic acid	256	4.92
21.598	1,3-Decosenoic acid	322	4.63
23.142	2-Hexadecen-1-ol	296	4.45
24.525	1-Decanol	158	3.36

2. 11. Gravimetric results

Gravimetric analysis was carried out to study the effect of time and concentration on the corrosion inhibition process. Figure 2 shows the variation of weight loss with time for mild steel corrosion in 1 M HCl (a) and 0.5 M H_2SO_4 (b) solutions in the absence and presence of SA extract and Figure 3 shows the variation of inhibition efficiency with concentration in 1 M HCl (a) and 0.5 M H_2SO_4 (a) in the absence and presence of 1000 mg/L SA extract. Figures 2 (a) and (b) indicate that weight loss increased with time for mild steel corrosion in the absence and presence of SA extract indicating that the corrosion process depends on exposure time. Figure 3 shows that the inhibition efficiency increased with extract concentration. The result indicates that the extract was an effective additive at all the concentrations studied, the inhibition efficiency can be seen to maintain a steady rate at all concentrations. The inhibition efficiency from the gravimetric data was calculated with the following formula.

$$IE(\%) = 1 - \frac{\Delta W_{inh}}{\Delta W_{blank}}$$

.........(1)

where ΔW_{inh} and ΔW_{blank} are the weight loss of mild steel in the presence and absence of inhibitor respectively [36].
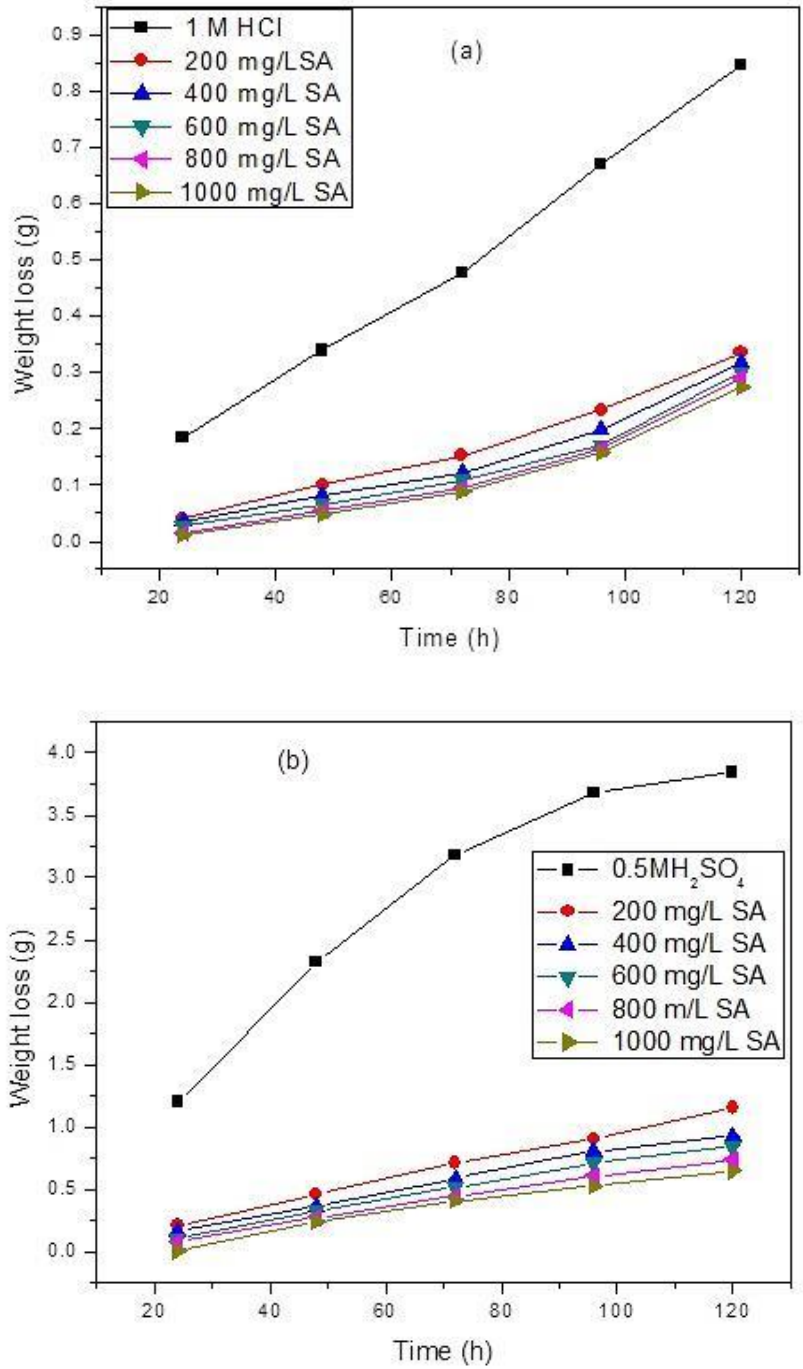

Figure 2. Variation of weight loss with time for mild steel corrosion in **(a)** 1 M HCl and **(b)** 0.5 M H2SO4 without and with SA extract.
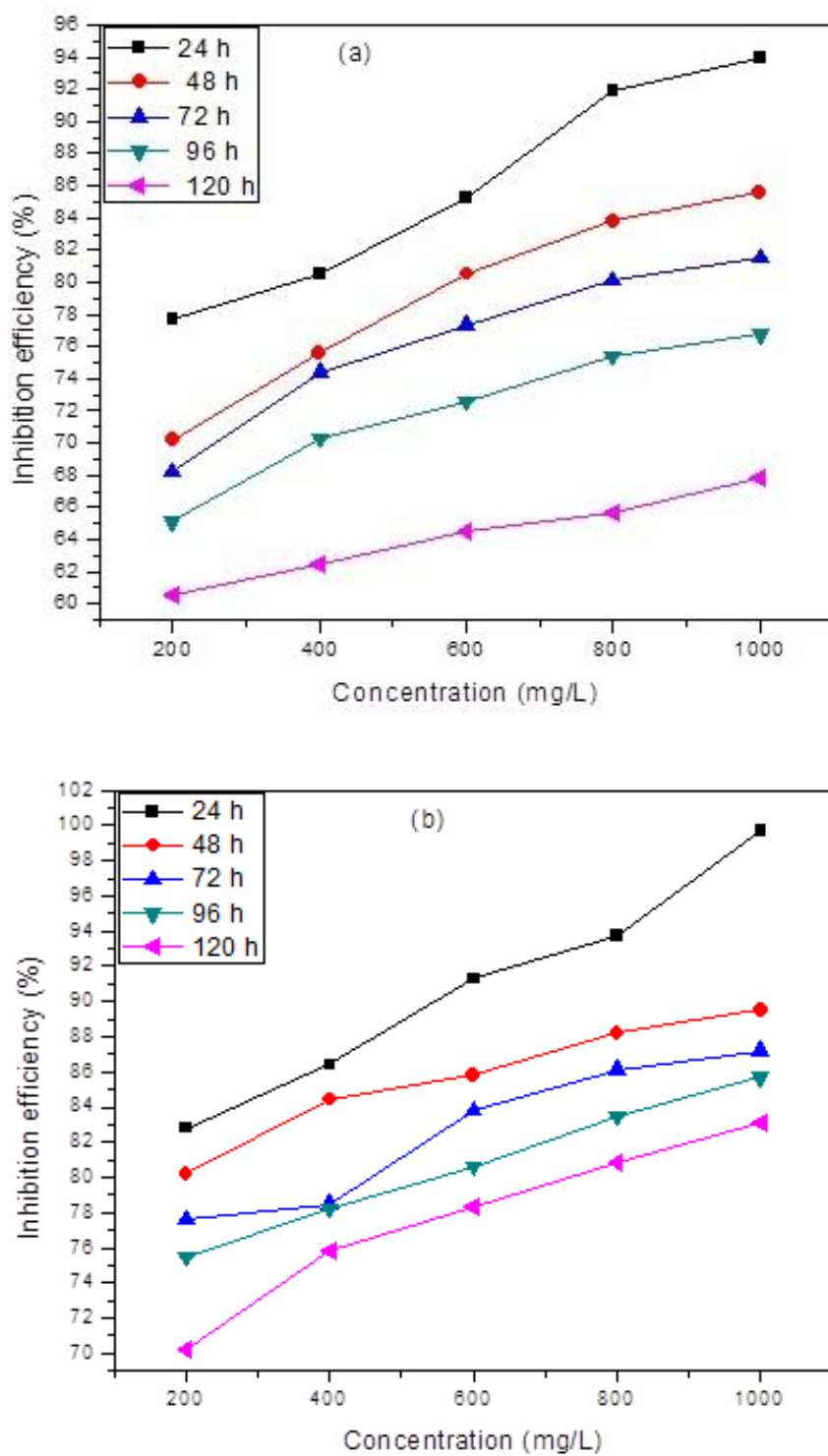
Figure 3. Inhibition efficiency vs concentration for mild steel corrosion in **(a)** 1 M HCl and **(b)** 0.5 M H₂SO₄ solutions.

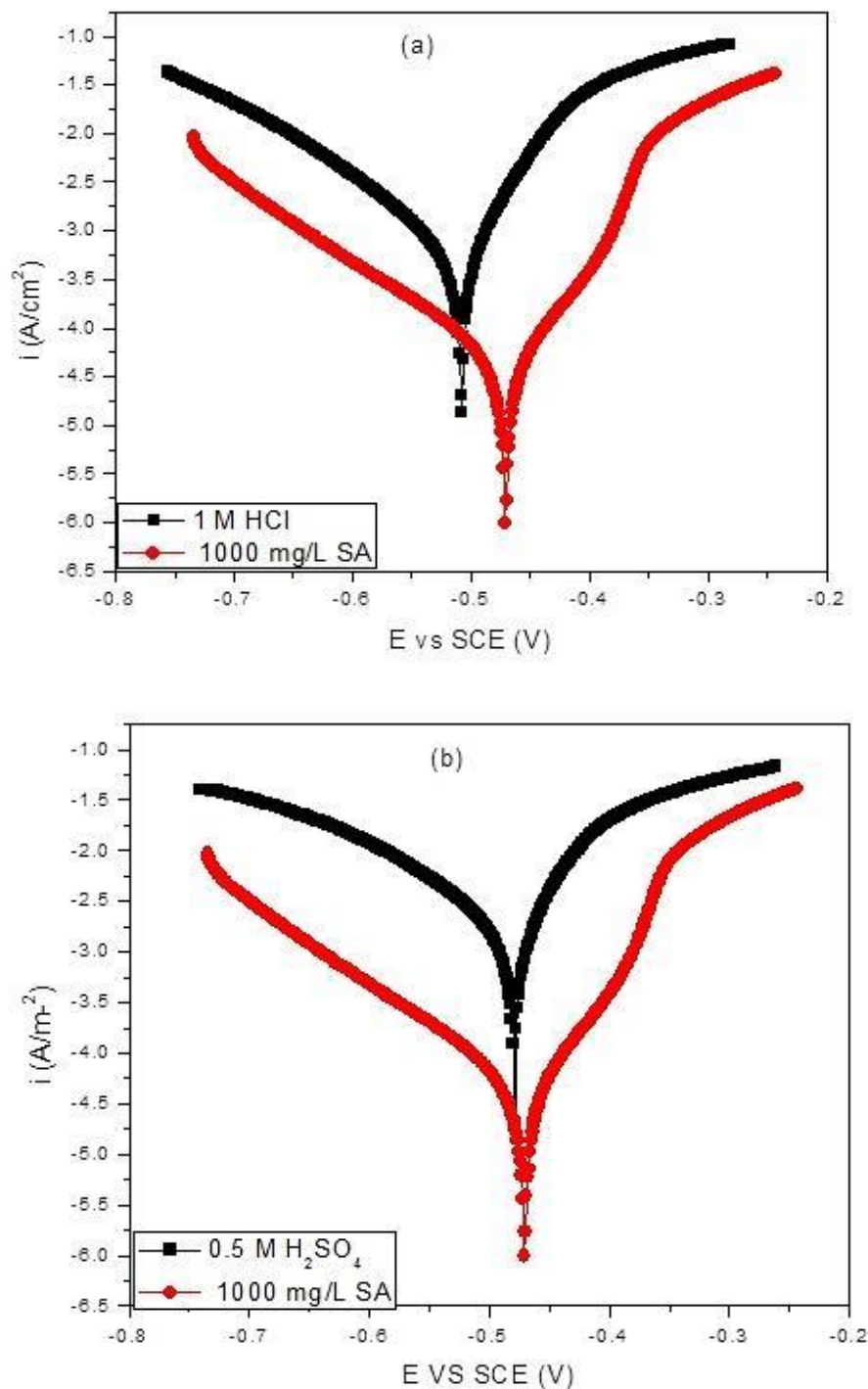**2. 12. Potentiodynamic polarization result**

Figure 4. Potentiodynamic polarization curves for mild steel corrosion in **(a)** 1 M HCl and **(b)** 0.5 M H₂SO₄ without and with SA extract.

To distinguish the effect of SA extract on the anodic and cathodic half reactions, potentiodynamic polarization experiment was undertaken. The potentiodynamic polarization curves for mild steel corrosion in 1 M HCl (a) and 0.5 M H_2SO_4 (b) are shown in Figure 4. The electrochemical parameters from the potentiodanamic polarization measurements are shown in Table 3. The result indicate that SA extract affected both the anodic dissolution of the metal and the cathodic reduction of hydrogen ions [37,38], the extract shifted the corrosion potential (Ecorr) slightly towards the more positive values reducing the anodic and cathodic current densities and also the corrosion current density (i_{corr}). The results indicate that SA extract functioned as a mixed type corrosion inhibitor affecting both the anodic and cathodic half reactions. The inhibition efficiency was calculated from the potentiodynamic polarization data using the formula below

$$IE(\%) = \left(\frac{I_{corr(bl)} - I_{corr(inh)}}{I_{corr(bl)}}\right) \times 100 \qquad \text{....... (2)}$$

where $I_{corr(bl)}$ and $I_{corr(inh)}$ represent the corrosion current densities in the absence and presence of SA.

Table. 3 Potentiodynamic polarization parameters for mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 with and without SA extract.

System (mg/L)	E mV (vs SCE)	i_{corr} (µA/cm²)	IE%
1 M HCl	-508.3	456.8	
1000 SA	-457.2	0.23	99.9
0.5 M H₂SO₄	-639.2	3570	
1000 SA	-473.1	36.5	99.0

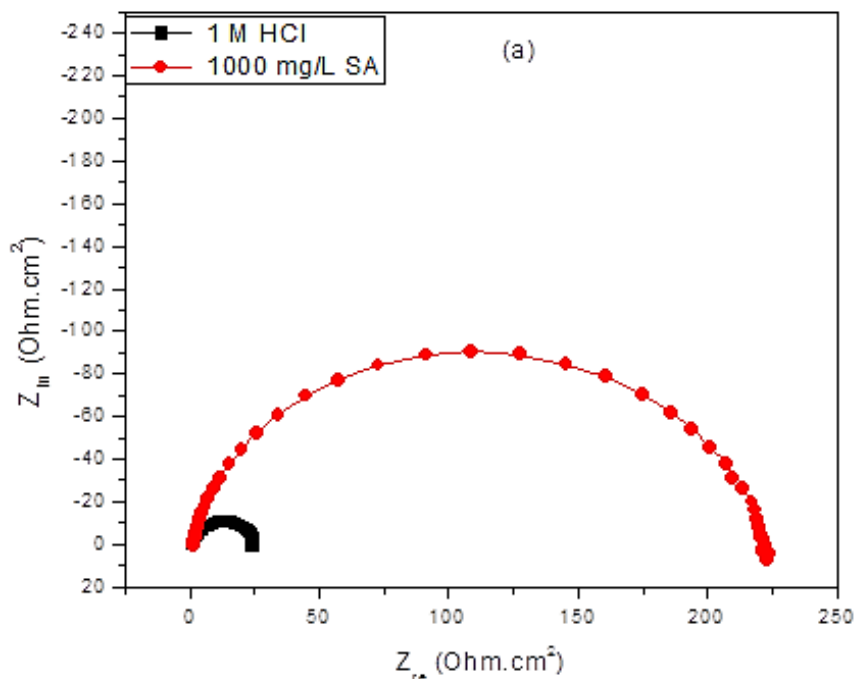## 2. 13. Electrochemical impedance spectroscopy (EIS) result

Electrochemical impedance spectroscopy experiments were undertaken to give insight into the kinetics of the electrochemical reactions. Nyquist plots for mild steel corrosion in the absence and presence of 1000 mg/L SA extract in 1 M HCl (5a) and 0.5 M H_2SO_4 (b) solutions are shown in Figure 5 while the electrochemical parameters from the (EIS) experiments are shown in Table 4. The Nyquist plots is seen to comprise of only one depressed capacitive semicircle in the high frequency region [36,37] typical for solid metal electrodes that show frequency dispersion of the impedance data [38]. The high frequency intercept with the real axis is designated as the solution resistance (R_s) while the low frequency intercept with the real axis is designated as the charge transfer resistance (R_{ct}). The impedance data was calculated by fitting the impedance spectra into an equivalent circuit

model R_s $(Q_{dl}R_{ct})$ which has been used previously to analyze impedance spectra [36]. The size of the Nyquist semicircle can be seen to have increased with the addition of SA. Table 4 shows gradual decrease in the size of the double layer capacitance (Q_{dl}) with the addition of SA. The decrease in the size of (Q_{dl}) may be attributed to the adsorption of SA constituents on the mild steel surface. Addition of the SA extract increased the charge transfer resistance (R_{ct}) values; this effect is attributed to increase in the size of the semicircle mentioned earlier. The inhibition efficiency from the impedance data was calculated using the formula below:

$$IE(\%) = \left(\frac{R_{ct,inh} - R_{ct,bl}}{R_{ct,inh}}\right) x\ 100 \tag{3}$$

Table 4 Impedance Results for mild steel Corrosion in 1 M HCl and 0.5 M H_2SO_4 without and with SA extract.

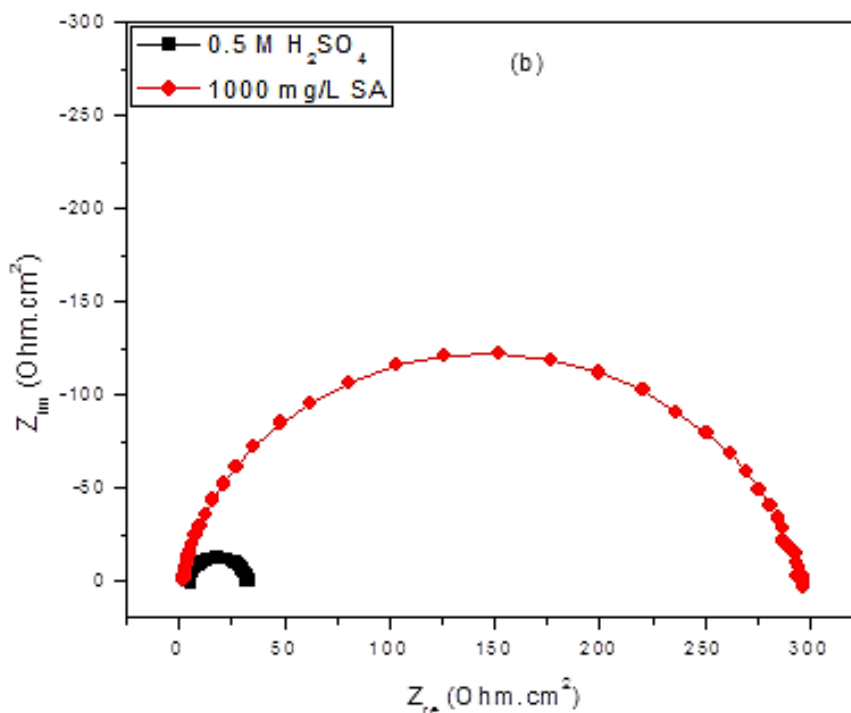| System (mg/L)	R_{ct} (Ωcm^2)	Q_{dl} $(\mu\Omega^{-1}S^ncm^{-2})$ $\times 10^{-6}$	IE(%)
1 M HCl	23.46	13.5	
1000 SA	218.5	3.65	89.3
0.5 M H2SO4	9.788	12.9	
1000 SA	290.8	3.45	96.6

Figure 5. Electrochemical impedance spectroscopy curves for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M H$_2$SO$_4$ without and with SA extract.

2. 14. Fourier transform infrared spectroscopy results

FTIR experiment was carried out to ascertain the functional groups present in the SA extract. The FTIR spectra of SA extract is shown in Figure 6. The result revealed some functional groups, The frequency 3339.7 indicates RO-H(Alcohol) wide rounded broad band , the frequency of 3011.7 broad corresponds to C-H aromatic ring, C-H functional group was shown by the frequency range of 2855.1-2922.2, the frequency of 17369 which corresponds to C=O functional group was also observed, the broad band 1617.7 indicates C=C functional group.

The broad band (1457 cm^{-1}) corresponds to the C-H alkyl functional group. The frequency 1337.9 indicates the presence of NO$_2$ group in the SA extract. The functional group of C=O was shown by the frequency of 1030 broad band. The presence of OH, –C=C- and C=O functional groups in SA extract suggests that it will be a good corrosion inhibitor for mild steel in acidic media [39].
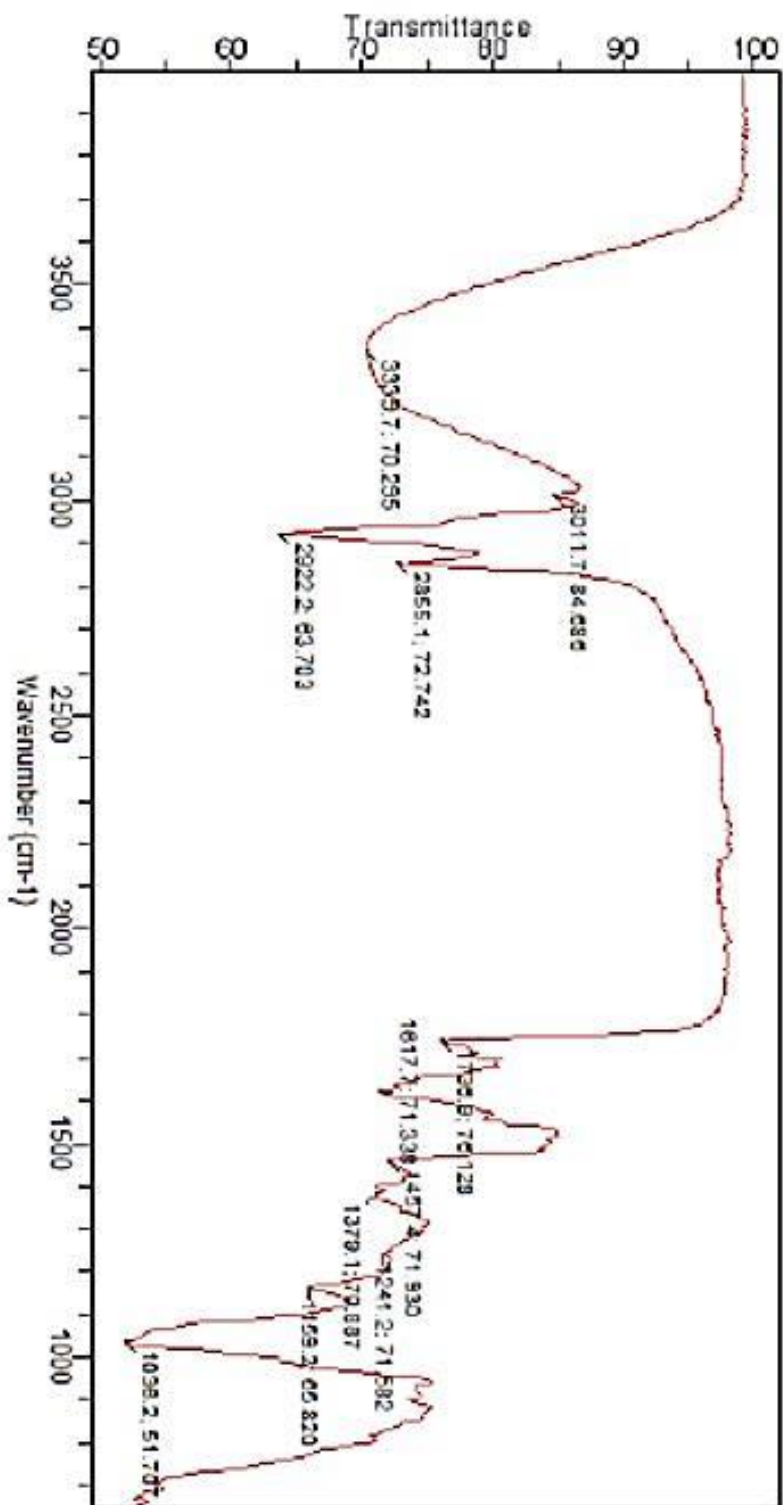
Figure 6. FTIR spectra of *Sida acuta* extract.
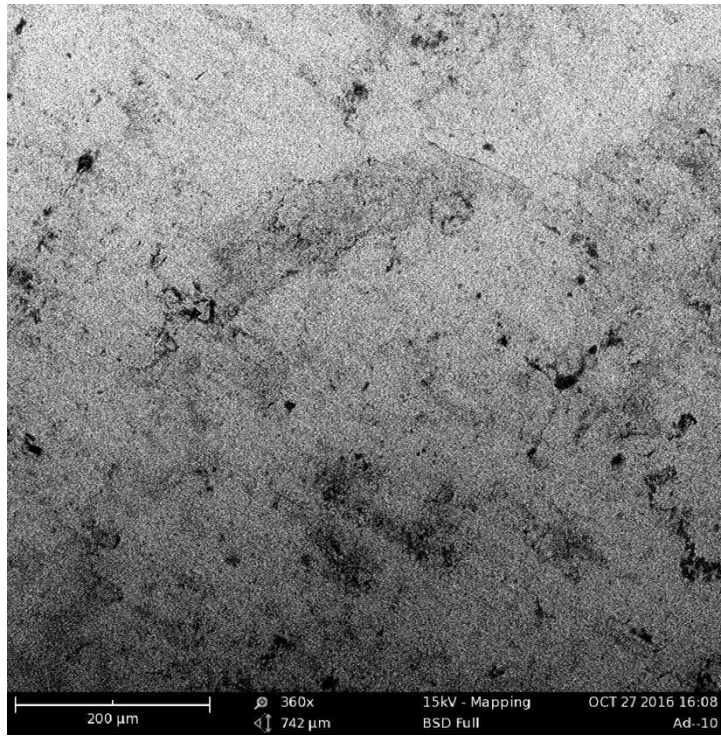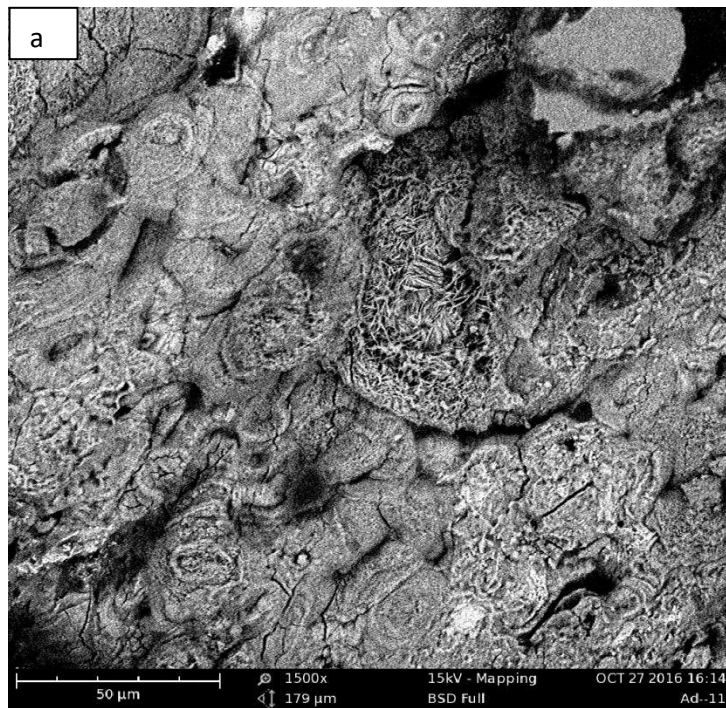
2. 15. Scanning electron microscopy results

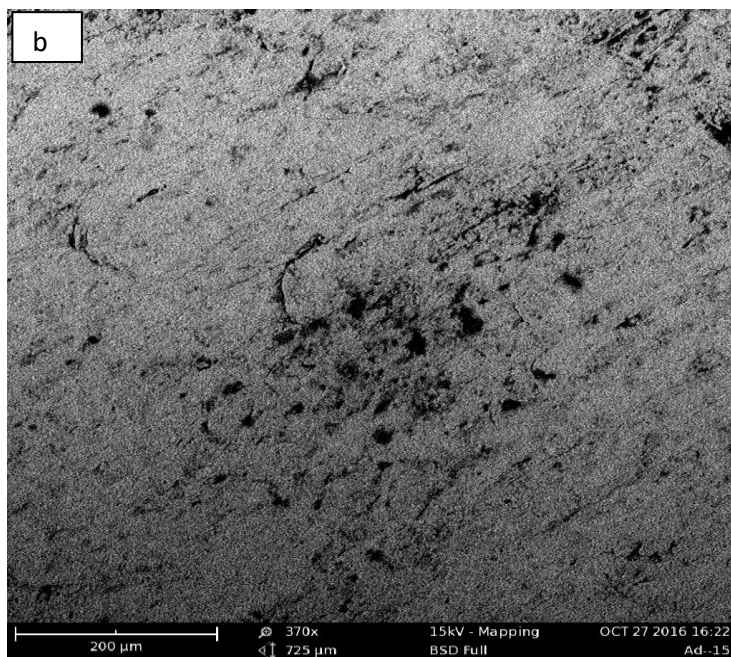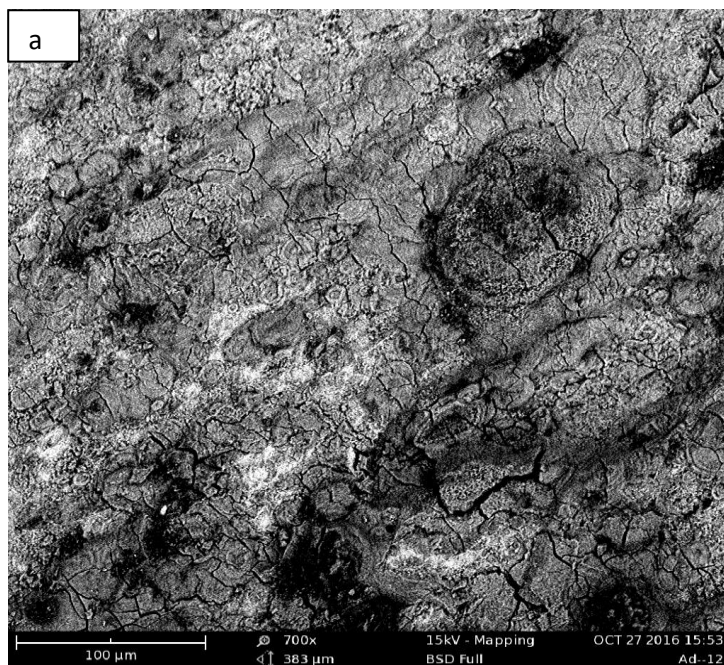**Figure 7**. Mild steel specimen before immersion in the acidic solutions

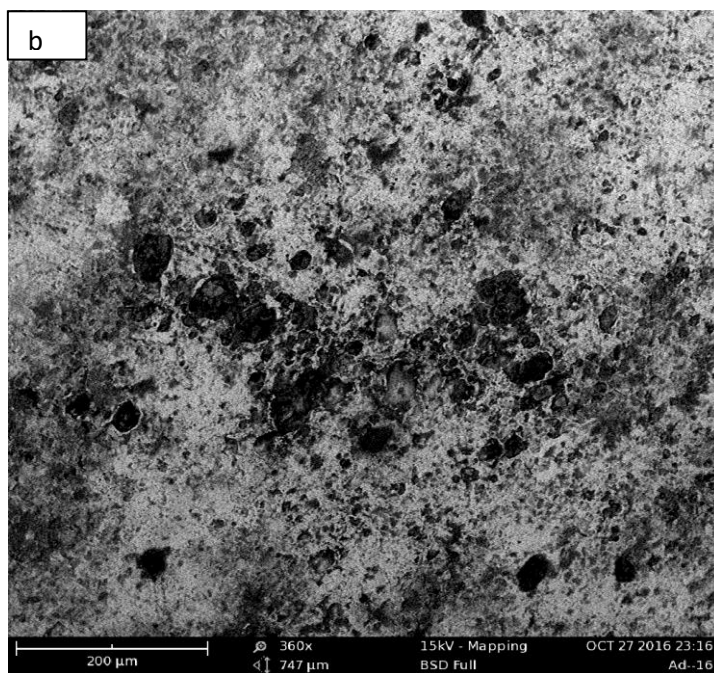**Figure 8.** SEM micrograph of mild steel specimen after 3-h immersion in 1 M HCl without **(a)** and with 1000 mg/L SA **(b)**

Figure 9. SEM micrograph of mild steel specimen after 3-h immersion in 1 M H_2SO_4 without (a) and with 1000 mg/L SA **(b)**

Scanning electron microscopy examination was performed on the mild steel specimen before and after immersion in 1 M HCl and 0.5 M H_2SO_4 solutions for 3-h and in the acidic solutions containing 1000 mg/L of the acids. Figure 7 shows the SEM image of the plan mild steel before immersion in the acidic solutions, Figure 8 show the SEM image of the mild steel specimen after 3-himmersion in 1 M HCl in the absence of SA (8a) and presence of 1000 mg/L SA (8b) and Figure 9 presents the SEM image of the metal after 3-h immersion in 0.5 M H_2SO_4 in the absence of SA (9a) and in the presence of 1000 mg L SA (9b). The result show severely corroded surfaces in the blank solutions while the surfaces in the solution containing SA were smooth, this may be attributed to the rapid dissolution of the metal in the acidic solutions in the absence of SA extract.

3. CONCLUSION

The research investigated the extract constituents and the corrosion inhibiting ability of *Sida acuta* leaves using phytochemical, Gas-mas chromatography, gravimetric, electrochemical and scanning electron microscopy methods. The phytochemical screening result indicate the presence of Alkaloids, Flavonoids, Saponins, Phenols and tannins in a the SA extract, the gravimetric results showed that SA reduced the corrosion of mild steel in the studied aggressive solutions, the electrochemical result showed that SA inhibited both the

anodic and cathodic half reactions while scanning electron microscopy revealed severely corroded metal without the SA inhibitor.

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