# Corrosion Inhibition of Mild steel in 1N HCl Media by Acid Extract of *Spathodea Campanulata* Leaves

## K. Shanmuga Priya[1], V.G. Vasudha[2]

[1]*(Department of Chemistry, BNMIT, Bangalore, VTU, Belgaum, Karnataka, India).*
[2]*(Department of Chemistry, Nirmala College for women, Coimbatore, Tamilnadu, India).*

***Abstract:*** *Inhibition of corrosion of mild steel in HCl solution by Spathodea Campanulata (SC) leaf extract has been studied by gravimetric, polarization, electrochemical impedance measurements and temperature studies. Inhibition efficiency was found to increase with increasing concentration of the extract. The effect of temperature (35-75°C) and immersion time on the corrosion behavior of mild steel in 1 N hydrochloric acid on addition of extract was also studied. The inhibitor molecules were found to get adsorbed on the metal surface obeying Langmuir, Temkin, Freundlich adsorption isotherms. Polarization studies showed that the extract of SC behaved as a very good mixed type inhibitor inhibiting both anodic and cathodic reaction. A maximum inhibition efficiency of 84.5% was obtained at an inhibitor concentration of 1.5% (v/v). Surface analysis was done by scanning electron microscope technology (SEM) to study the nature of adsorption.*

***Keywords:*** *Corrosion inhibitor, Mild steel, Spathodea Campanulata, Polarization, HCl medium*

## I. Introduction

Mild steel one of the most widely used metals in most of the industries are most often exposed to the action of acids during industrial process such as acid cleaning, descaling and acid pickling. This has led to corrosion of mild steel proving the necessity for an inhibitor [1-4]. Corrosion of metals can be controlled by many methods but using an inhibitor is the best among all the methods. A number of organic compounds are being used as corrosion inhibitor for mild steel in acidic medium. Such compounds contain nitrogen, oxygen or sulphur groups which gets adsorbed on the metal surface and act as a barrier to corrosion [5]. But because of the toxic nature and high cost, use of natural product as corrosion inhibitor is drawing lots of attention [6]. Corrosion inhibitors obtained from plants are cheap, biodegradable and less toxic as they do not contain heavy metals[7]. Anticorrosion activity of Embilica officianilis, Terminalica chebula, sapindus trifolianus, Swertia angustifolia, Eucalyptus leaves, Eugenia jambolans, Pongamia glabra, Annona squamosa, Accacia Arabica, Carica papaya, Azadirachta indica, Veronia amydalina and Nyctanthes arbortristis on mild steel has been reported [8-18]. The present study explains the corrosion inhibition activity of Spathodea Campanulata on mild steel using gravimetric and electrochemical techniques.

## II. Experimental

### A. Preparation of Samples and test solutions

Fresh green leaves of Spathodea Campanulata (SC) were collected washed and shade dried and powdered. 25g of this powder was weighed and added to 500ml of 1N HCl. This mixture was refluxed for three hours and kept overnight. The following day it was filtered and the filtrate was made up to 500ml using 1N HCl. This was taken as the stock solution. The required concentrations were prepared by diluting the stock solution.

Mild steel sheets cut into rectangular coupons of size 5 X 1cm$^2$ provided with holes to enable suspension in test solutions were used for the study. These steel pieces were mechanically polished to remove any rust on it. The metal pieces were then degreased with acetone washed with distilled water and polished with emery paper, cleaned, dried and stored in desiccators. Mild steel coupons with 1 cm$^2$ exposed area were used as working electrode for electrochemical studies.

### B. Weight loss method

Metal samples were weighed using electronic balance. Weighed rectangular coupons of the metal samples were immersed in triplicate in 100mL of 1N HCl with different concentrations of plant extract (0.1%, 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, 1.3% and 1.5% v/v) and without plant extract (Blank). After 1 hour immersion in the test solution the coupons were removed washed, dried and weighed. The experiment was carried out at different immersion periods (1 Hr, 2 Hr, 5 Hr, 7 Hr, 12 Hr and 24 Hr). Weight loss was measured for all the above mentioned timings at 303K. Corrosion inhibition studies were also carried out at different temperatures (308, 318, 328, 338 and 348K). After measuring the weight loss, surface coverage ($\theta$) and percentage inhibition efficiency (IE %) were calculated using the following formula

$\theta$ = (IE % / 100);

IE % = $\dfrac{w_0 - w_i}{w_i}$ X 100; (Where $w_0$ and $w_i$ are weight loss without and with plant extract respectively.)

### C. Electrochemical study (TAFEL and EIS)

A conventional three electrode glass cell consisting of a working electrode (mild steel sample), a pure platinum counter electrode and a saturated calomel reference electrode was used for the measurements. The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. All tests were performed in unstirred conditions at 303 K using CH1660D electrochemical workstation. The working electrode was maintained at open circuit conditions for 1 Hr and thereafter anodic and cathodic polarization curves were recorded in the potential range from -800 to +500 mV with a scan rate of 0.4 mV s$^{-1}$. The AC impedance measurements were performed in the frequency range of 0.1 to 10,000 Hz with signal amplitude of 10mV.

### D. Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The surface morphology of the mild steel specimen was evaluated by SEM-EDX analysis with. Mild steel samples immersed in 1 N HCl, lowest inhibitor concentration and highest inhibitor concentrations were examined for the above study.

## III.     Results And Discussion

Weight loss measurement was performed in 1N HCl in presence and absence of extract at 303K for different immersion periods from 1 Hr to 24 Hr. Fig.1 shows a plot of IE% with different timings. Inhibition efficiency increases from 1 hour to 24 hours (Table I) which shows the strong adsorption of constituents present in the plant extract on the surface of mild steel giving it a protective layer. From this it is clearly shown that leaves of Spathodea Campanulata acts as a very good corrosion inhibitor for mild steel in 1N HCl solution.

**Table I:** % IE Of SC in HCl At Different Concentrations And Different Immersion Periods

| Time In hr | % IE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **0.1** | **0.3** | **0.5** | **0.7** | **0.9** | **1.1** | **1.3** | **1.5** |
| 1 | 30.00 | 32.00 | 44.00 | 54.00 | 60.00 | 64.00 | 72.00 | 74.00 |
| 2 | 33.33 | 36.84 | 47.37 | 59.65 | 63.16 | 68.42 | 73.68 | 75.44 |
| 5 | 36.44 | 39.83 | 53.39 | 61.86 | 65.25 | 73.31 | 75.42 | 78.81 |
| 7 | 38.51 | 46.62 | 55.41 | 64.86 | 69.59 | 77.03 | 79.05 | 80.41 |
| 12 | 42.94 | 48.99 | 56.15 | 67.52 | 73.76 | 78.35 | 80.92 | 82.20 |
| 24 | 48.24 | 50.82 | 59.25 | 69.09 | 75.41 | 80.56 | 82.44 | 84.54 |
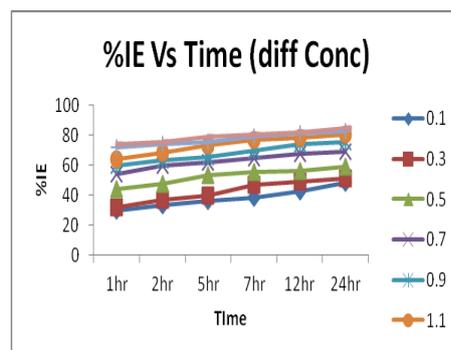


**Fig .1**: Plot of % IE Vs Time different concentrations

Weight loss measurement was carried out at different temperatures (308 – 348K) in presence and absence of the inhibitor to evaluate the stability of the adsorbed film on the mild steel piece. This was done for a period of 1 Hour each. The results obtained are shown in Table II. Fig .2 depicts that as the temperature increases the inhibition efficiency decreases. At elevated temperature as time lag between adsorption and desorption of inhibitor over metal surface becomes shorter the IE decreases. Metal surface remaining exposed to acid environment for a longer period increases the rate of corrosion and thus decreases the inhibition efficiency.

**Table II:** % IE Of SC in HCl At Different Concentrations And Different Temperatures

| Temp In K | % IE | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 | 1.1 | 1.3 | 1.5 |
| 308 | 35.29 | 47.06 | 52.94 | 56.86 | 62.75 | 66.67 | 72.55 | 78.43 |
| 318 | 34.07 | 45.19 | 51.85 | 54.81 | 60.74 | 64.44 | 70.37 | 77.04 |
| 328 | 33.05 | 44.14 | 50.21 | 53.14 | 59.62 | 63.18 | 69.04 | 76.15 |
| 338 | 31.88 | 42.28 | 48.60 | 51.54 | 56.18 | 62.78 | 67.13 | 74.30 |
| 348 | 29.02 | 40.17 | 46.50 | 49.53 | 54.35 | 60.40 | 65.41 | 72.31 |
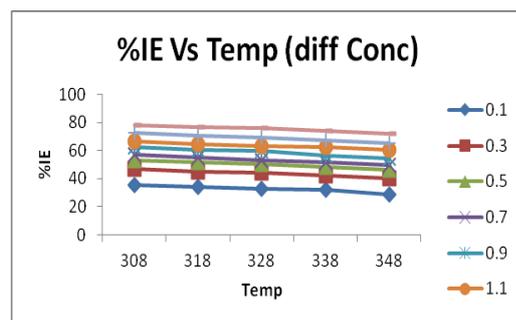


**Fig .2** Plot of % IE Vs Temp different Conc.

Corrosion rate (CR) of mild steel in the absence and presence of SC extract was calculated and the data obtained for different temperatures are shown in Table III. Plots of corrosion rates against different temperatures are shown in Fig 3.

**Table III:** CR OF SC IN HCL At Different Concentrations And Different Temperatures

| Extract Conc. (%v/v) | CR | | | | |
|---|---|---|---|---|---|
| | 308 K | 318 K | 328 K | 338 K | 348 K |
| **Blank** | 222.4085 | 588.7283 | 2084.534 | 3104.996 | 4613.885 |
| **0.1** | 143.9114 | 388.1246 | 1395.504 | 2115.061 | 3275.073 |
| **0.3** | 117.7457 | 322.7103 | 1164.374 | 1792.35 | 2760.481 |
| **0.5** | 104.6628 | 283.4618 | 1037.906 | 1596.108 | 2468.298 |
| **0.7** | 95.9409 | 266.018 | 976.8528 | 1504.528 | 2328.747 |
| **0.9** | 82.85805 | 231.1304 | 841.6634 | 1360.616 | 2106.339 |
| **1.1** | 74.13615 | 209.3256 | 767.5272 | 1155.652 | 1827.238 |
| **1.3** | 61.0533 | 174.438 | 645.4206 | 1020.462 | 1596.108 |
| **1.5** | 47.97045 | 135.1895 | 497.1483 | 798.0539 | 1277.758 |
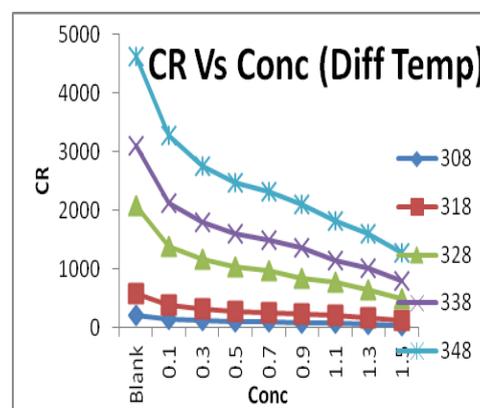


**Fig .3**: Plot of CR Vs concentration at different temperatures

The result obtained shows that the rate of corrosion of mild steel decreases with increase in the concentration of SC extract but increases with increase in temperature. This confirms the inhibitive action of the extract in HCl medium.

The Arrhenius equation was employed to study the effect of temperature on the rate of corrosion of mild steel in HCl containing various concentrations of SC extract as expressed by

$$CR = A\, e^{-Ea/RT}$$

Where CR is the corrosion rate of mild steel, A is Arrhenius or pre-exponential factor, $E_a$ is the activation energy, R is the gas constant and T is the temperature.

A plot of log of corrosion rate obtained by gravimetric measures against 1/T gave a straight line as shown in Fig 4.with a slope of $-E_a / 2.303R$, where $E_a$ is the activation energy.

The activation energies in the presence of inhibitors may be higher, equal to or lower than those in the absence of the inhibitor[19]. In the present study, it could be seen that $E_a$ is more in the presence of inhibitor. Increase in $E_a$ in presence of inhibitor is attributed to an appreciable increase in the adsorption process of the inhibitor on the steel surface with increase in temperature. This also indicates corresponding decrease in reaction rate as the surface is less exposed to acid in presence of inhibitor.

The values of $E_a$ (activation energies) obtained from the slope of the straight line are listed in Table IV.

**Table IV:** Activation Energy Values For Different Concentrations Of SC IN HCL

| Conc. Of plant Extract ( %v/v) | $E_a$     KJ/mol |
|---|---|
| **Blank** | 69.36 |
| **0.1** | 71.29 |
| **0.3** | 72 |
| **0.5** | 72.22 |
| **0.7** | 72.79 |
| **0.9** | 73.95 |
| **1.1** | 72.85 |
| **1.3** | 74.42 |
| **1.5** | 74.8 |
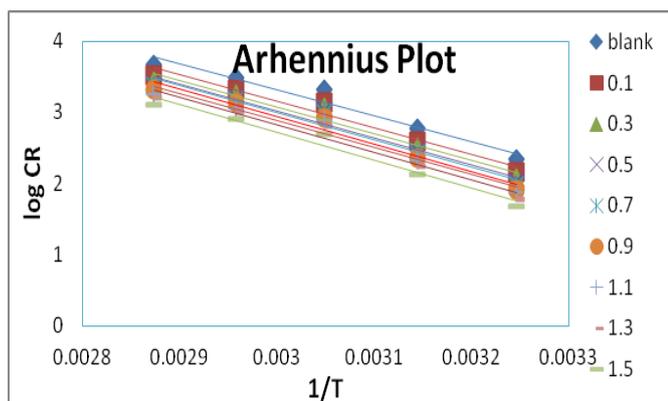


**Fig 4**: Arrhenius plot (log CR vs 1/T) for SC extract in HCl

The interaction between inhibitor and mild steel surface can be understood from the adsorption isotherms. The values of surface coverage ($\theta$) were evaluated using CR values obtained from the weight loss method. The values of surface coverage at different concentrations of Spathodea Campanulata leaves extract in HCl media in temperature range of 308 K to 348 K is used to explain the adsorption process. The $\theta$ values for different concentration of inhibitors from the acid were tested graphically by fitting to various isotherms. It was observed that the data fitted the Langmuir, Temkin and Freundlich adsorption isotherms with correlation coefficients >0.9.
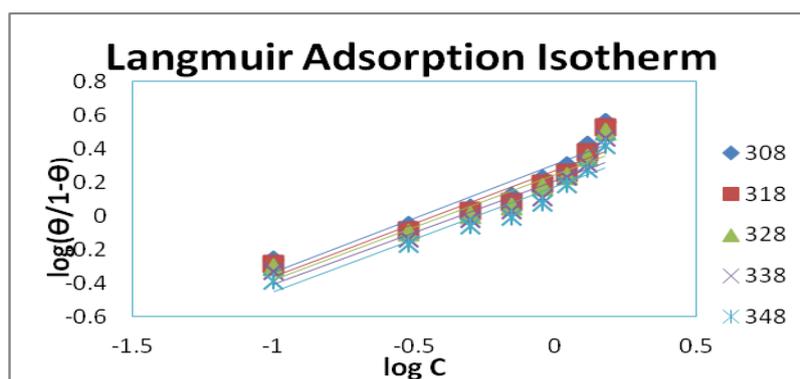


**Fig .5**  Langmuir isotherm of SC in HCl

The plots of log($\theta$ /1- $\theta$ ) vs log C yielded a straight line, where C is the inhibitor concentration, proving that the inhibition is due to the adsorption of the active compounds onto the metal surface and obeys the Langmuir isotherm which is shown in Fig .5. From the results obtained, it is significant to note that these plots are linear with the slopes equal to unity, which indicates a strong adherence of the adsorption data to the assumptions confirming Langmuir adsorption isotherm.

The potentiodynamic polarization data are shown as the Tafel plots for mild steel in 1N HCl with the addition of various concentrations of the inhibitor in Fig.6. The corrosion kinetic parameters such as corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), anodic and cathodic Tafel slopes ($b_a$ and $b_c$) were derived from these curves and are given in Table V. The % IE was calculated using the formula

$$\%IE = \frac{I_{corr\ (blank)} - I_{corr\ (inh)}}{I_{corr\ (blank)}} * 100$$

Where $I_{corr\ (blank)}$ and $I_{corr\ (inh)}$ are the values of corrosion current densities of mild steel without and with the inhibitor respectively, which was determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential $E_{corr}$. The values given in the Table V shows that corrosion current ($I_{corr}$) decreases markedly in the presence of extract, which confirms the inhibitive action of SC extract in HCl medium. The anodic and cathodic Tafel slopes $b_a$ and $b_c$ are changed markedly in the presence of the extract, which confirms that the extract contained the active molecules which behaved as mixed-type of acid corrosion inhibitors.
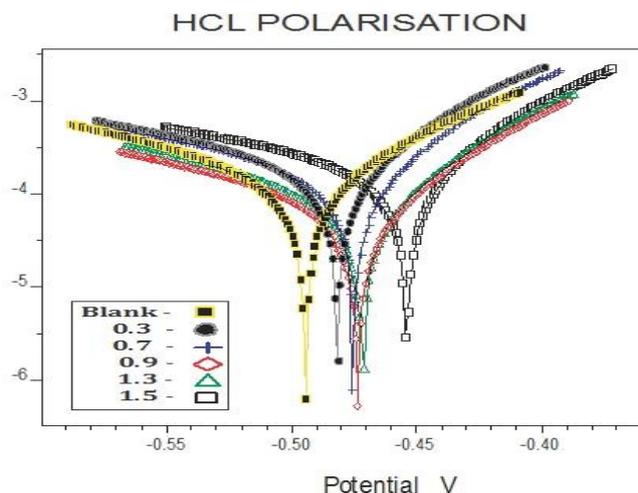
## HCL POLARISATION



**Fig. 6:** Potentiodynamic polarization of mild steel in 1N HCl with and without SC extract

**Table V:** Potentiodynamic Polarization Parameters For Mild Steel In 1N HCL IN Presence OF SC Extract.

| Conc | $E_{corr}$ | $I_{corr}$ | $b_a$ | $b_c$ | $R_p$ | % IE | |
|---|---|---|---|---|---|---|---|
| % v/v | V | mAmp/cm$^2$ | mV/dec | mV/dec | ohm/cm$^2$ | Tafel | Linear |
| Blank | -0.4788 | 0.171 | 58 | 141 | 133.6 | _ | _ |
| 0.3 | -0.452 | 0.1592 | 59 | 145 | 146 | 6.900585 | 8.493151 |
| 0.7 | -0.4725 | 0.141 | 57 | 137 | 158.5 | 17.54386 | 15.70978 |
| 0.9 | -0.4921 | 0.13 | 71 | 120 | 191.3 | 23.97661 | 30.16205 |
| 1.3 | -0.4672 | 0.0765 | 57 | 125 | 285 | 55.26316 | 53.12281 |
| 1.5 | -0.4686 | 0.0651 | 58 | 125 | 336.6 | 61.92982 | 60.30897 |

The inhibitive properties of the extract have also been evaluated by the determination of the polarization resistance $R_p$. The linear polarization values $R_p$ in the absence and presence of different concentrations of inhibitor are given in the Table V. The % IE was calculated as follows

$$\% \text{IE} = \frac{R_{p\,(inh)} - R_{p\,(blank)}}{R_{p\,(inh)}} * 100$$

Where $R_{p\,(inh)}$ and $R_{p\,(blank)}$ are linear polarization values in presence and absence of inhibitor. From the results, $R_p$ values gradually increased with increase in the concentration of inhibitor confirming that the extracts of SC acted as a good corrosion inhibitor.

The corrosion behavior of mild steel in 1N HCl in the absence and presence of different concentrations of SC extract were also investigated by Electrochemical Impedance Spectroscopy (EIS) technique. The resultant Nyquist plots are shown in Fig.7. The existence of single semicircle in each plot shows that there was only single charge transfer process during the anodic dissolution of MS. There was a gradual increase in the diameter of each semicircle of the Nyquist plot due to increase in the number of inhibitive molecules in the extract when the concentration was raised from 0.1 to 1.5 % v/v.
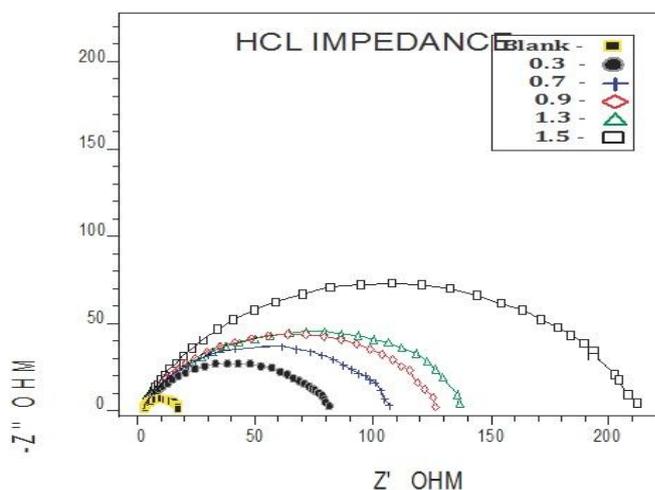


**Fig.7 :** Nyquist plot showing inhibitive effect of SC extract on corrosion of mild steel in 1N HCl.

From the values obtained in Table VI the $R_{ct}$ values increased with the increasing concentration of the inhibitor indicating that more inhibitor molecule adsorb on the metal surface at higher concentration and form a protective film on the metal-solution interface. The values of $C_{dl}$ decreased with increasing inhibitor concentration. Decrease of $C_{dl}$ indicates a reduction in local dielectric constant by increase in thickness of the electrical double layer. Thus the results obtained indicate that the extract of SC function by adsorption on the metal surface causing a decrease in the $C_{dl}$ values and an increase in the $R_{ct}$ values

**Table VI:** Impedance Parameters For Mild Steel IN 1N HCL IN The Presence OF SC Extract.

| Conc | $C_{dl}$ | $R_{ct}$ | Inhibitor Efficiency |
|---|---|---|---|
| % v/v | µ farads | ohms | Linear |
| Blank | 63.9 | 11.06 | |
| 0.3 | 58.3 | 61.06 | 81.88667 |
| 0.7 | 56.8 | 82.7 | 86.62636 |
| 0.9 | 48.2 | 98.71 | 88.79546 |
| 1.3 | 42.6 | 103.41 | 89.30471 |
| 1.5 | 27.8 | 168.4 | 93.4323 |

The SEM micrographs of different slides of mild steel after immersion in the aqueous solution with the absence and presence of the inhibitor are shown in Fig.8 and Fig.9.
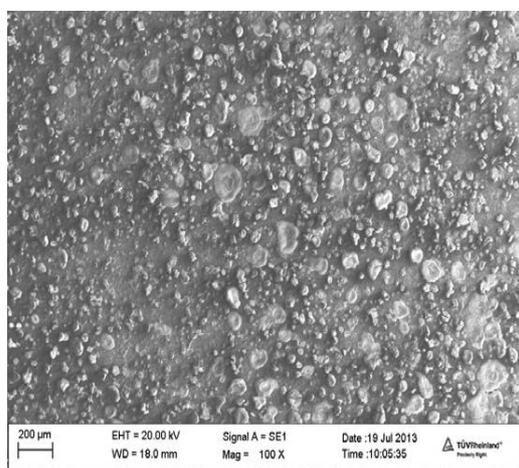


**Fig. 8** SEM images of MS in 1 N HCl
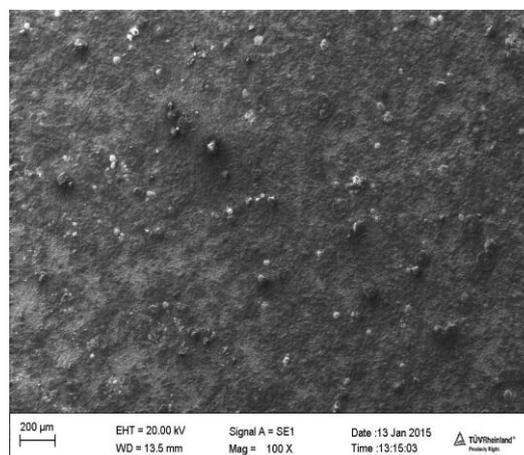


**Fig .9** SEM images of MS with 1.5% (v/v) SC extract.

The SEM images in Fig.8 shows that the surface of mild steel was extremely damaged in the absence of the extract while Fig. 9 shows the formation of a film by the constituents present in leaf extract of Spathodea Campanulata (SC) on the mild steel surface which was responsible for corrosion inhibition.

## IV. Conclusion

Spathodea Campanulata leaf extract acted as a very good corrosion inhibitor for mild steel in 1 N HCl solution due to the formation of a layer on the metal surface. Increase in concentration increased the inhibition efficiency and the results obtained from potentiodynamic polarization measurements showed that the extract of SC leaves acted as a mixed type inhibitor inhibiting both anodic and cathodic reactions. Results obtained from gravimetric studies were in good agreement with that obtained from electrochemical studies which support the above discussion. Thus acid extract of SC leaves is considered to be a cheap, eco-friendly and effective corrosion inhibitor for mild steel in acid media.

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