SYNERGISTIC EFFECT OF CALOTROPIS PLANT IN CONTROLLING CORROSION OF MILD STEEL IN BASIC SOLUTION

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ABSTRACTS

The alcoholic extracts of leaves, latex and fruit from the *Calotropis procera* and *Calotropis gigantea* are tested for corrosion inhibition in basic solution by mass loss method and thermometric method. In the present investigation the extract reduces the corrosion rate of mild steel in basic solution. The inhibition efficiency increases as the extract concentration is increased. The alcoholic extract of Calotropis is found effective corrosion inhibitor in basic media and give up to 80.89% efficiency.

Key words: Mild steel, Mass loss method, Thermometric, Corrosion, Adsorption.

INTRODUCTION

Mild steel is widely used in chemical industries due to its low cost and easy availability for fabrication reaction of vessel, tanks, pipeline and boiler, because it suffer from severe corrosion in aggressive environments, it has to be protective. The corrosion of metal in aqueous solution occurs in two steps oxidation and reduction. Oxidation reaction takes place at anode, whereas reduction takes place at cathode. The cathodic reaction may be either by evolution of hydrogen and absorption of oxygen.

Mild steel is a reactive metal to reduce the corrosion problem in these environment inhibitive effects of various naturally occurring substance like *Datura stramonium*[1], *Tannin beet* root, *Tamarind*, *Tealeaves*, *Pomegranate juice*, *Saponin*[2], *Embellica officinalis*, *Terminalia bellerica*, a mixture of the later three *Spindus trifolianus*, *Acacia concianna*, *Swerti aungustifolia* and quinoline based cinchona alkaloids as well as very popular ayurvadic powder *Mahasudarshana churna*, *Prosopis juliflora*[3], *Caparis decidua*[4], *Adhotoda-vasica*, *Vinca-rosea*, *Heena*[5], *Eugenia jambolans*, *pomegranate* and *Peels*[6-7], *Tannins*, *Caffeine*, *Prosopis cineraria*[8] and *Ficus relegeosa*[9] have been evaluated as effective corrosion inhibitor. *Calotropis* is used as a traditional medicinal plant with unique properties. *Calotropis* is used alone or with other medicinalis to treat common disease. Generally organic compounds having heteroatom O, N and S are found to have basicity and electron density thus assist in corrosion inhibitor. O, N and S are the active center for the adsorption on the metal surface[10-11].

Mass loss can be determined gravimetrically, volumetrically and radiometrically, all are the direct measures of corrosion of these, gravimetrically or mass loss methods are most used for inhibitor testing.

EXPERIMENTAL

The Calotropis extract was obtained by dried, then finally powdered and extracted with boiling ethanol. The solvent is distilled off and the residue is treated with the inorganic acid where the base is extracted as their soluble salts. The free acids are liberated by the addition of base and extracted with various solvents, e.g. chloroform etc. The mixture of bases thus obtained is separated by various methods into the individual compounds. To clean the stuff obtained it was boiled with activated charcoal (2gm) to remove gung and pure plant extract was obtained.

(a) Specimen preparation:

Rectangular specimens of mild steel of dimension 2.5*1.5*0.02Cm^3 containing a small hole of 0.2Cm diameter near the upper edge were employed for the determination of corrosion rate. Specimens were cleaned by buffing to produce a mirror finish with the help of pumic powder and degreased. Each specimen was suspended by a glass hook and immersed in a beaker containing 50mL of test solution at 23$^{\cdot C}$ and left exposed to air to 24 hours. Evaporational losses were made up with deionized water. After the test specimens were cleaned with benzene. Duplicate experiments were performed in each case and mean values of the mass loss were calculated.

(b) Test solution preparation:

The basic solution was prepared by using deionized water. All chemicals were used of analytical reagent quality.

The percentage inhibition efficiency was calaulated as[12]

I=100(ΔMu–ΔMi/ΔMu) ----------------------------- (1)

Where ΔMu and ΔMi are the mass loss of the metal is uninhibited and inhibited solution respectively.

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

θ= ΔMu–ΔMi/ΔMu -------------------------------------- (2)

Where θ surface coverage and ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited basic solution.

The corrosion rate is mmpy (mili meter penetration per year) can be obtained by the following equation

Corrosion rate (mmpy) = Weight loss*87.6/Area*Time*Metal density ------ (3)

where mass loss is expressed in gm, area is expressed in cm² of metal surface exposed, time is expressed in hours of exposure, metal density is expressed in gm/cm³and 87.6 is conversion factor.

Inhibition efficiency was also determined using a thermometric technique. This involved the immersion of single specimens measuring 2.5*1.5*0.02 Cm^3 in a reaction chamber containing 50 Ml of test solution. Temperature changes were measured at interval of one minute using a thermometer with a precision of 0.5$^{\circ C}$.The temperature increased slowly at first then rapidly and attained a maximum temperature was recorded percentage inhibition efficiencies were calculated as[13]

η=100(RN$_{free}$-RNi)/RN$_{free}$ ---------------------------- (4)

Where RN$_i$ and RN$_{free}$ are the reaction number in the presence and absence of inhibitors respectively and RN ($^{\circ C}$/min) is defined as

RN=(Tm-To)/t -- (5)

Where Tm and To are the maximum and initial temperature respectively and t is the time required to reach the maximum temperature.

RESULT AND DISCUSSION

The inhibition efficiency (%) calculated from the mass loss measurement for sodium hydroxide solution and inhibitors are given in tables (1-4). It is observed that the inhibition efficiency increases with increase in the concentration of inhibition and decreases with increases in acid strength. The corrosion rate decreases with increases in concentration of inhibitor. The maximum efficiency was obtained in low acid concentration. The inhibitors have shown the efficiency in the range. Calotropis procera show minimum 31.77% and maximum 78.95% whereas latex shows minimum 33.41% and maximum 80.18% but fruit shows 32.19% minimum and 79.88% maximum for 0.5M sodium hydroxide solution instead of Calotropis gigantean shows

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minimum 31.35% and maximum 78.57% whereas latex shows minimum 33.88% and maximum 80.89% but fruit shows 33.44% minimum and 80.33% maximum for 0.5M sodium hydroxide solution but Calotropis procera in 1M sodium hydroxide solution show minimum 50.09% and maximum 79.16% with leaves while latex shows minimum 48.05% and maximum 79.92% whereas fruit shows minimum 49.95% and maximum 78.97% inhibition efficiency instead of Calotropis gigantea show minimum 31.35% and maximum 80.89% inhibition efficiency with leaves extract but latex reveals 48.53% minimum and 79.68 maximum efficiency and fruit shows 50.37% minimum and 79.37% maximum inhibition efficiency towards sodium hydroxide solution.

Table-1. Mass loss data for mild steel in 0.5M sodium hydroxide acid with ethanolic extract of leaves, latex and fruit of Calotropis procera.

Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 24 hours.

Inhibitor Concentration (%)	Mass loss (mg)	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
Uninhibited	3412		21.0	
Leaves				
0.12	2328	31.77	14.3	0.3177
0.24	2043	40.12	12.6	0.4012
0.36	1656	51.46	10.2	0.5146
0.48	1269	62.80	7.84	0.6280
0.60	718	78.95	4.43	0.7895
Latex				
0.12	2272	33.41	14.0	0.3341
0.24	1938	43.20	11.9	0.4320
0.36	1541	54.83	9.52	0.5483
0.48	1154	66.17	7.13	0.6617
0.60	676	80.18	4.18	0.8018
Fruit				
0.12	2289	32.91	14.1	0.3291
0.24	2022	40.73	12.5	0.4073
0.36	1643	51.84	10.1	0.5184
0.48	1134	66.76	7.01	0.6676
0.60	688	79.83	4.25	0.7983

Table-2. Mass loss data for mild steel in 0.5M sodium hydroxide acid with ethanolic extract of leaves, latex and fruit of Calotropis gigantea.

Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 24 hours.

Inhibitor Concentration (%)	Mass loss (mg)	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
Uninhibited	3412		21.0	
Leaves				
0.12	2342	31.35	14.0	0.3135
0.24	2061	39.59	12.7	0.3959
0.36	1634	52.11	10.1	0.5211
0.48	1245	63.51	7.69	0.6351
0.60	731	78.57	4.52	0.7857
Latex				
0.12	2256	33.88	13.9	0.3388
0.24	1942	43.08	12.0	0.4308
0.36	1527	55.24	9.44	0.5524
0.48	1134	66.76	7.01	0.6676
0.60	652	80.89	4.03	0.8089
Fruit				
0.12	2271	33.44	14.0	0.3344
0.24	2045	40.06	12.6	0.4006
0.36	1623	52.43	10.0	0.5243
0.48	1152	66.23	7.12	0.6623
0.60	671	80.33	4.14	0.8033

Table-3. Mass loss data for mild steel in 1.0M sodium hydroxide acid with ethanolic extract of leaves, latex and fruit of Calotropis procera. Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 24 hours.

Inhibitor Concentration (%)	Mass loss (mg)	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
Uninhibited	4518		27.9	
Leaves				
0.12	2250	50.09	13.9	0.5009
0.24	1934	57.19	11.9	0.5719
0.36	1746	61.35	10.7	0.6135
0.48	1360	69.89	8.40	0.6989
0.60	921	79.16	5.69	0.7916
Latex				
0.12	2347	48.05	14.5	0.4805
0.24	1918	57.54	11.8	0.5754
0.36	1763	60.97	10.9	0.6097
0.48	1332	70.51	8.23	0.7051
0.60	907	79.92	5.60	0.7992
Fruit				
0.12	2261	49.95	13.9	0.4995
0.24	1945	56.94	12.0	0.5694
0.36	1734	61.62	10.7	0.6162
0.48	1326	70.65	8.19	0.7065
0.60	950	78.97	5.87	0.7897

Table-4. Mass loss data for mild steel in 1.0M sodium hydroxide acid with ethanolic extract of leaves, latex and fruit of Calotropis gigantea. Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 24 hours.

Inhibitor Concentration (%)	Mass loss (mg)	Inhibition efficiency (%)	Corrosion rate (mmpy)	Surface coverage (θ)
Uninhibited	4518		27.9	
Leaves				
0.12	2231	50.61	13.7	0.5061
0.24	1952	56.79	12.0	0.5679
0.36	1725	61.81	10.6	0.6181
0.48	1343	70.27	8.30	0.7027
0.60	941	79.17	5.81	0.7917
Latex				
0.12	2325	48.53	14.3	0.4853
0.24	1932	57.23	11.9	0.5723
0.36	1744	61.39	10.7	0.6139
0.48	1351	70.09	8.35	0.7009
0.60	918	79.68	5.67	0.7968
Fruit				
0.12	2242	50.37	13.8	0.5037
0.24	1923	57.43	11.8	0.5743
0.36	1718	61.97	10.6	0.6197
0.48	1345	70.23	8.31	0.7023
0.60	932	79.37	5.76	0.7937

Inhibition efficiency values were also determined by the thermometric method (Tables 5-6). Temperature changes for mild steel in 3M, 4M and 5M sodium hydroxide solution were recorded at various inhibitor concentrations. However, no significance temperature changes were obtained for 1M and 2M sodium hydroxide solution. Therefore, the thermometric method was used for 3M, 4M and 5M sodium hydroxide solution. For lower concentration of sodium hydroxide solution have lower reaction number but inhibition efficiency is higher instead of higher concentration has its vice-versa. Calotropis procera leaves extract show minimum inhibition efficiency 28.26% and 71.73% but latex shows minimum 21.73% and maximum 73.91% while fruit shows minimum 26.08% and 76.08% maximum inhibition efficiency for 3M sodium hydroxide solution. Calotropis procera leaves extract show minimum inhibition efficiency 36.84% and 73.68% but latex shows minimum 34.73% and maximum 71.57% while fruit shows minimum 38.94% and 75.78% maximum inhibition efficiency for 4M sodium hydroxide solution. Calotropis procera leaves extract show minimum inhibition efficiency 33.33% and 70.73% but latex shows minimum 30.08% and maximum 66.66% while fruit shows minimum 34.95% and 73.14% maximum inhibition efficiency for 5M sodium hydroxide solution instead of Calotropis gigantea leaves extract show minimum inhibition efficiency 30.43% and 78.26% but latex shows minimum 23.91% and maximum 73.91% while fruit shows minimum 28.26% and 80.43% maximum inhibition efficiency for 3M sodium hydroxide solution. Calotropis gigantea leaves extract show minimum inhibition efficiency 38.94% and 75.78% but latex shows minimum 35.78% and maximum 72.63% while fruit shows minimum 42.10% and 76.84% maximum inhibition efficiency for 4M sodium hydroxide solution. Calotropis gigantea leaves extract show minimum inhibition efficiency 34.14% and 72.35% but latex shows minimum 31.70% and maximum 68.39% while fruit shows minimum 35.77% and 73.98% maximum inhibition efficiency for 5M sodium hydroxide solution.

Table–5. Thermometric reactions for mild steel in sodium hydroxide with ethanolic extract of Leaves, Latex and Fruit of Calotropis *procera*. Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 0.5 hours.

Inhibitor Concentration (%)	Reaction number (3M)	Inhibition Efficiency (%)	Reaction number (4M)	Inhibition Efficiency (%)	Reaction number (5M)	Inhibition Efficiency (%)
Uninhibited	4.6		9.5		12.3	
Leaves						
0.12	3.3	28.26	6.0	36.84	8.2	33.33
0.24	2.8	39.13	4.7	50.52	7.6	38.21
0.36	2.2	52.17	3.9	58.94	6.4	47.96
0.48	1.8	60.86	3.1	67.36	5.0	59.34
0.60	1.3	71.73	2.5	73.68	3.6	70.73
Latex						
0.12	3.6	21.73	6.2	34.73	8.6	30.08
0.24	3.0	34.78	5.0	47.36	7.8	36.58
0.36	2.4	47.82	4.2	55.78	6.7	45.52
0.48	1.9	58.69	3.4	64.21	5.3	56.91
0.60	1.2	73.91	2..7	71.57	4.1	66.66
Fruit						
0.12	3.4	26.08	5.8	38.94	8.0	34.95
0.24	29	36.95	4.4	53.68	7.1	42.27
0.36	2.3	50.00	3.8	60.00	6.3	48.78
0.48	1.5	67.39	3.0	68.42	4.8	60.97
0.60	1.1	76.08	2.3	75.78	3.3	73.17

Table–6. Thermometric reactions for mild steel in sodium hydroxide with ethanolic extract of Leaves, Latex and Fruit of Calotropis *gigantea*. Effective area of specimen: 3.75 cm^2. Temperature: 23 ± 0.1°C. Immersion Time: 0.5 hours.

Inhibitor Concentration (%)	Reaction number (3M)	Inhibition Efficiency (%)	Reaction number (4M)	Inhibition Efficiency (%)	Reaction number (5M)	Inhibition Efficiency (%)
Uninhibited	4.6		9.5		12.3	
Leaves						
0.12	3.2	30.43	5.8	38.94	8.1	34.14
0.24	2.7	41.30	4.5	52.63	7.4	39.83
0.36	2.1	54.34	3.8	60.00	6.2	49.59
0.48	1.5	67.39	3.0	68.42	4.9	60.16
0.60	1.0	78.26	2.3	75.78	3.4	72.35
Latex						
0.12	3.5	23.91	6.1	35.78	8.4	31.70
0.24	2.9	36.95	4.9	48.42	7.6	38.21
0.36	2.3	50.00	4.1	56.84	6.5	47.15
0.48	1.7	63.04	3.3	65.26	5.1	58.53
0.60	1.2	73.91	2.6	72.63	3.9	68.39
Fruit						
0.12	3.3	28.26	5.5	42.10	7.9	35.77
0.24	2.8	39.13	4.3	54.73	7.0	43.08
0.36	2.2	52.17	3.9	58.94	6.1	50.40
0.48	1.4	69.56	3.1	67.31	4.7	61.78
0.60	0.9	80.43	2.2	76.84	3.2	73.98

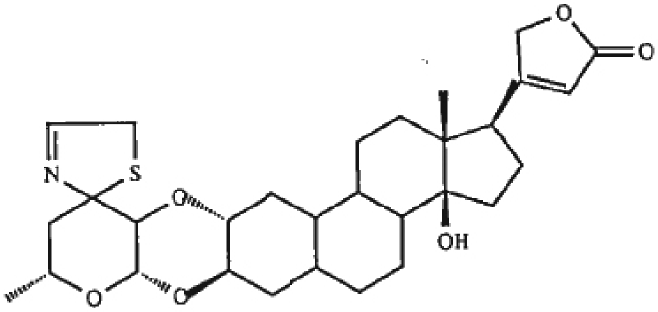


Figure-1. Uscharin

Generally the adsorption of organic molecules involves O, N and S atoms. This process may block active sites hence may decrease the corrosion rate. In that the plant extract uscharin adsorbed on the metal surface and decreases the surface area available for cathodic and anodic reaction to take place. In the present study it is assumed that the plant extract are adsorbed on the metal surface and decreases the surface area available for cathodic and anodic reaction to take place. The nitrogen, sulphur and oxygen of uscharin may be responsible for the adsorption. Organic inhibitors, with active portions contain generally large C-H chains or rings with positively charged amine nitrogen group at the one end.

Organic corrosion inhibitors[14] may function as:

1.- Chemisorption of the molecule on the metallic surface.
2.- Complexing of the molecule with the metal ion which remains in solid state.
3.- Neutralising the corrodant.
4.- Adsorbing the corrodent.

They offered large coverage due to the long hydrocarbon chain and by the presence of OH group, being hydrophilic in nature; the OH group counteracted the effects of chain length and ensured higher solubility.

Cathodic inhibitors slow down the reaction taking place at cathode (i.e. H_2 evolution)

eg. organic inhibitors like amine, substituted urea's, heavy metal soap etc. decrease H_2 evolution process. Mild steel salts deposits on cathode helps in decreasing the O_2 absorption process.

Absorption of oxygen: This type of corrosion occurs generally in aqueous solution.

AT ANODE- Fe --------→ $Fe^{2+} + 2e^-$ (Oxidation) ------- **(6)**

AT CATHODE $\frac{1}{2} O_2 + H_2O + 2e^-$ -----→ $2OH^-$ (Reduction) ---- **(7)**

The Fe^{2+} and OH^- ions diffuse towards each other (Smaller Fe^{2+} diffuse more rapidly) and forms $Fe(OH)_2$

$Fe^{2+} + 2OH^-$ ----------→ $Fe(OH)_2$ -------------------------- **(8)**

If oxygen is present

$Fe(OH)_2 + O_2 + 2 H_2O$ ----------→ $Fe(OH)_3$ -------------- **(9)**

Yellow rust

If oxygen is less, then it forms black Fe_3O_4 (Anhydrous magnetite)

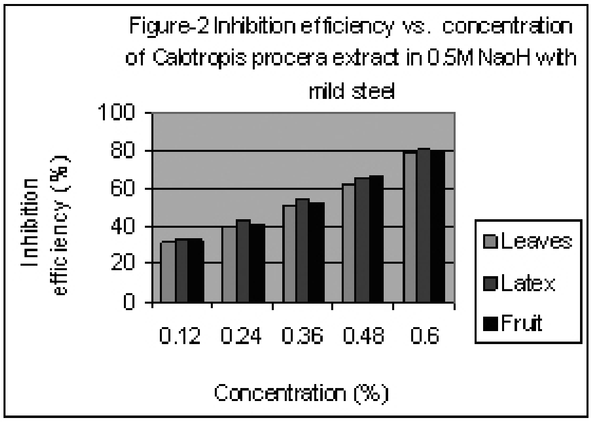
If oxygen absorption type of corrosion, the anodic area are small, while the cathodic are large.

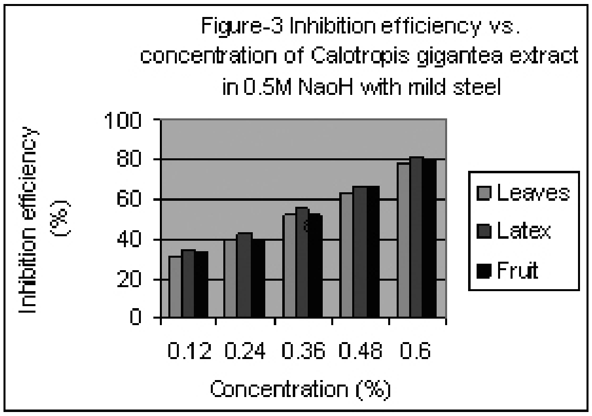
Mild steel when exposed to alkaline solution, temperature and stress causes due to caustic embrittlement i.e. in experimental condition sodium hydroxide react with mild steel to form sodium ferroate. This decomposes and sodium hydroxide is regenerated which causes further dissolution of mild steel. All metal above hydrogen in electrochemical series have a tendency to get dissolve in solution releasing hydrogen.

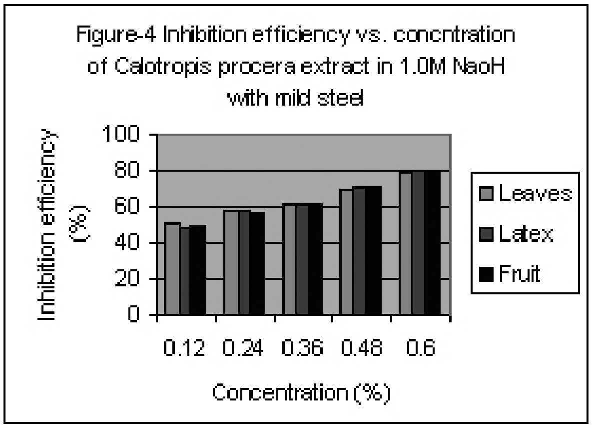
Figures (2-5) shows inhibition efficiency increases with increase in the concentration of inhibition and decrease with increase in acidic strength.

It has been observed that the fruit extract of *Calotropis procera* and *Calotropis gigantea* has maximum inhibition efficiency compared to the leaves and latex extracts. This process increased the adsorptivity of the fruit extract on the corroding site of the metal. This explains that the higher inhibition efficiency displayed by the fruit extract for 0.6% concentration.

Figures (6-7) shows the surface analysis of metal by Scanning Electron Microscopy was carried out on Model- ZEISS EVO 50. The surface morphological characteristics of the blank and inhibited mild steel were analyzed at magnification of 2.0 KX operated at an accelerating voltage of 20 KV. Scanning electron microscopy reveals that plant extract adsorbed on metal surface that decreases the metal surface for corrosion attack. SEM provides a two-dimensional projection or a two-dimensional image of a sample.







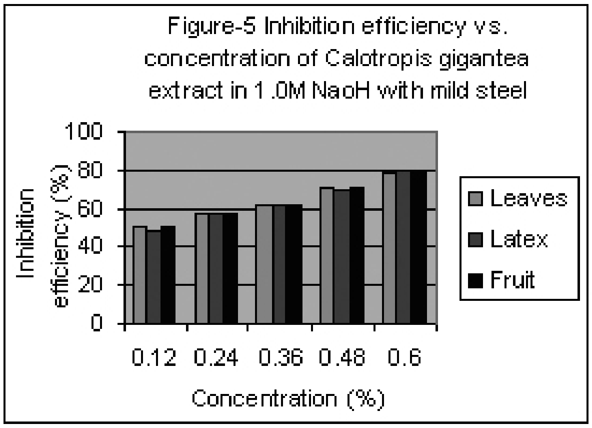


Figure- 6. Surface analysis of mild steel blank.

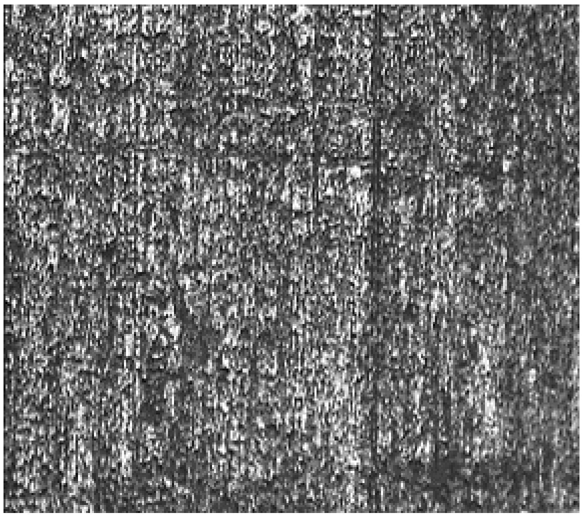


Figure- 7. Surface analysis of mild steel in 0.5M sodium hydroxide solution. in 0.5M sodium hydroxide solution with *Calotropis gigantea* latex.

CONCLUSIONS

1. Plant inhibitors inhibited mild steel corrosion in basic solutions.
2. Corrosion inhibition of mild steel in basic solution is under anodic control.
3. Inhibition efficiency of plant extracts increases with increase in concentration.
4. The mass loss measurements are in good agreement with electrochemical method.
5. The surface analysis has shown that inhibition of corrosion by plant extract is due to formation of layer on the mild steel surface.

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