Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **5(8),** 28-34, August **(2015)** *Res. J. Chem. Sci.*

Eco-Friendly Corrosion inhibition of Mild steel in Hydrochloric acid using *Leptadenia pyrotechnica* as a Green inhibitor

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Available online at: www.isca.in, www.isca.me
Received 26th July 2015, revised 3rd July 2015, accepted 18th August 2015

Abstract

Mass loss technique has been used to study the corrosion inhibition efficiency of mild steel in HCl solution by using the stem, fruit and root extract of Leptadenia pyrotechnica. The results show that all the extracts under study are good corrosion inhibitors, among which stem extract is the most effective. Corrosion inhibition efficiency increases with increasing concentration of inhibitor and it also increases with increasing concentration of HCl solution. Inhibition efficiency was found maximum up to 93.07% for mild steel with 0.8% stem extract.

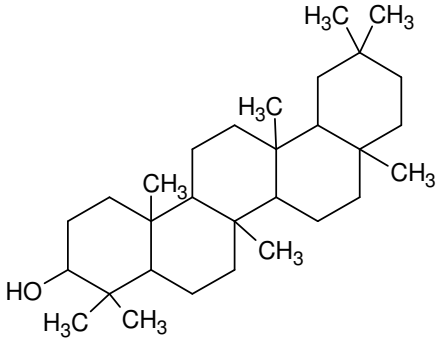
Keywords: Corrosion, mild steel, mass loss method, thermometric method, inhibition efficiency.

Introduction

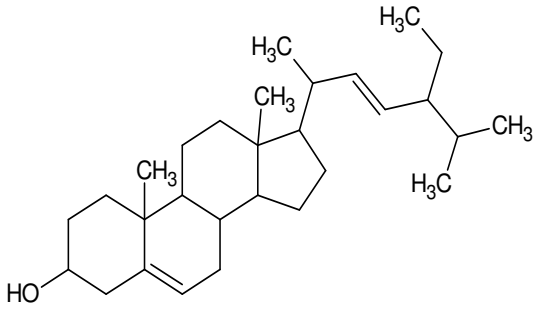
Mild steel is extensively used in different industries by virtue of its good structure, properties, mechanical workability and low cost. Acid solutions are used in the industrial processes, acid cleaning, acid descaling, acid pickling and oil well acidizing. Since it suffers severe corrosion in corrosive environment, it has to be protected. Presence of hetero atom (S, N and O) with free electron pairs, aromatic rings with delocalized π-electrons, alkyl chains with high molecular weight and substituent group in organic compound generally improve the inhibition efficiency[2]. It is noticed that organic compounds show higher inhibition efficiency as compared to inorganic. A number of naturally occurring substances like Henna, Tamarind, Tea leaves, Garlic, Beet-root, Pomegranate juice and peels, Eucalyptus leaves extract, Curry leave and very popular ayurvedic powder Mahasudarshana churna have been reported as corrosion combating material[2-8]. Corrosion inhibition efficiency of *Eugenia jambolana, Adhatoda vasica, Prosopis juliflora, Datura Stromonium, Hibiscus Cannabinus*[12]*, Ocimum sanctum, Cordia dichotoma* has also been reported. Recently the use of naturally occurring substances like Brahmi, Bhringaraj, Molasses, Pumpkins, Black tea, *Pennisetum glaucum, Allium cepa* and *Araucaria columnaris* have been evaluated as effective green corrosion inhibitors[9-22].

In the present studies the inhibitive effects of ethanolic extract of stem, fruit and root of *Leptadenia pyrotechnica* have been tested. *Leptadenia pyrotechnica* (common name – Kheep) is an erect, ascending shrub with green stem and pale green alternating bushy branches with watery sap.

Chemical constituents: Three terpenes (phytol, squalene and taraxerol), five sterols (cholesterol, campasterol, stigmasterol, β-sitosterol and fucosterol), fifteen fatty acids (C14-C25), eleven n-alkanol (C29-C39) has been isolated from extract of Leptadenia pyrotechnica [23]. Moustafa et al. reported the isolation of twenty four alkaloids and three glycoside from the aerial parts of the *Leptadenia pyrotechnica*[24]. Almost all of the alkaloids belonged to heterocyclic group including pyridine, pyrrole, pyrazine and indole types.



Taraxerol



Stigmasterol

Material and Methods

Mild steel having composition of 0.14% C, 0.11% Si, 0.35% Mn, 0.75%Ni, 0.025% P, 0.03% S and the rest of Fe, specimens used in the mass loss experiments were mechanically cut from commercially available mild steel samples into coupons of 2.5cm x 1.55cm x 0.02cm with a small hole of about 2mm diameter near the upper edge. Specimens were cleaned by buffing to produce spotless finish and then degreased. Different concentration solutions of hydrochloric acid were prepared using double distilled water.

The extract of stem, fruit and root of *Leptadenia pyrotechnica* were obtained by drying, then finely powdered and extracted with boiling ethanol. The solvent is distilled off and the residue is treated using inorganic acid, where the bases are extracted as their soluble salt. The free bases are librated by the addition of any bases and extracted with various solvents, e.g. ether, chloroform etc. Each specimen was suspended by a glass hook and immersed in a beaker containing 50 mL of test solution with or without inhibitor at room temperature and left exposed to air. Evaporation losses were made up with distilled water. Duplicate experiments were performed for each and mean values of mass loss were calculated. The percentage inhibition efficiency was calculated as-

$$\text{Inhibition efficiency } (\eta\ \%) = \frac{100(\Delta M_u - \Delta M_i)}{\Delta M_u} \quad (1)$$

Where ΔM_u and ΔM_i are the mass loss of the specimen in uninhibited and in inhibited solution respectively.

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

$$\text{Surface coverage } (\theta) = \frac{(\Delta M_u - \Delta M_i)}{\Delta M_u} \quad (2)$$

The corrosion rates in mmpy can be obtained by-

$$\text{Corrosion rate (mmpy)} = \frac{\text{Mass loss x } 87.6}{\text{Area x Time x Metal density}} \quad (3)$$

Where mass loss is expressed in mg. Area is expressed in cm^2. Exposed time is expressed in hours and metal density is expressed in gm/cm^3.

Inhibition efficiency was also calculated using thermometric method. This involves the immersion of specimen (dimension 2.5cm x 1.55cm x 0.02cm) in an insulating reaction chamber having 50 mL of test solution at an initial room temperature. Temperature change was observed at regular intervals using a thermometer with a precision of 0.1^0C. Initially the increase in temperature was slow, then rapid, attaining a maximum value and then decreased. The maximum temperature was noted. The inhibition efficiency was calculated as

$$\text{Inhibition efficiency } (\eta\ \%) = \frac{100(RN_f - RN_i)}{RN_f} \quad (4)$$

Where RN_f and RN_i are the reaction number in the free solution and inhibited solution respectively.

Reaction number RN ($K\ min^{-1}$) is given as:

$$RN = \frac{T_m - T_i}{t} \quad (5)$$

Where Tm and Ti are the maximum temperature of solution and in initial temperature of solution respectively. t is time required (in minutes) to attain maximum temperature.

The coefficient of correlations (r) between the inhibitor concentration and inhibition efficiency can be calculated by using the formula-

$$r = \frac{N\sum dx\,dy - (\sum dx)(\sum dy)}{\sqrt{N\sum dx^2 - (\sum dx)^2 [N\sum dy^2 - (\sum dy)^2]}} \quad (6)$$

Where x is inhibitor concentration and y is inhibition efficiency. N is number of test sample.

Results and Discussion

The corrosion rate and inhibition efficiency measured from mass loss method for mild steel in hydrochloric acid solution with and without inhibitor are given in table 1. It is observed that the inhibition efficiency increases with increase in the concentration of inhibitor from 0.2% to 0.8%. Stem, fruit and root extract of *Leptadenia pyrotechnica* exhibit maximum inhibition efficiency up to 93.07%, 90.61% and 90.06% respectively in 1.5 N HCl.

Reaction numbers (RN) and inhibition efficiency obtained by thermometric method are summarized in table-2. The results indicate that reaction number decreases with increasing concentration of inhibitor as well as that of acid. The maximum inhibition efficacies observed by thermometric measurement are 87.95%, 84.96% and 82.85% for the stem, fruit and root respectively. The value of correlation coefficient (r = 0.9748, 0.9984 and 0.9885) indicate that there is a high degree positive correlation between concentration and inhibition efficiency (η %), which proves that the inhibition efficiency increases with increase in the inhibitor concentration.

SEM Analysis: Figure-4 and figure-6 show almost same view of surface whereas figure-5 shows immense roughness which depicts that the mild steel surface has been adversely affected in HCl. Corrosion has been almost inhibited by extract of *Leptadenia pyrotechnica* which is indicated by almost same view of mild steel surface (figure-4 and figure-6).

Conclusion

The alcoholic extracts of *Leptadenia pyrotechnica* are found to be effective green inhibitor in acid media giving up to 93.07% efficiency and can safely be used as eco-friendly corrosion combating material.

Table–1

Mass loss data for mild steel in HCl with alcoholic extracts of plant *Leptadenia pyrotechnica* at 299 ± 0.1K (Area of exposure – 7.75cm^2)

Plant part	Inhibitor Concen. (%)	0.5N HCl			1.0N HCl			1.5N HCl		
		Mass Loss (Δm) Mg	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)	Mass Loss (Δm) mg	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)	Mass Loss (Δm) mg	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)
Stem	Blank	775	-	15.4972	826	-	16.5170	895	-	17.8967
	0.2	103	86.71	2.0596	139	83.17	2.7795	117	86.92	2.3396
	0.4	93	88.00	1.8597	104	87.41	2.0796	94	89.50	1.8797
	0.6	75	90.32	1.4997	96	88.38	1.9196	83	90.73	1.6597
	0.8	61	92.13	1.2198	72	91.28	1.4397	62	93.07	1.2398
Fruit	Blank	775	-	15.4972	826	-	16.5170	895	-	17.8967
	0.2	325	58.06	6.4988	321	61.14	6.4188	195	78.21	3.8993
	0.4	279	64.00	5.5790	283	65.73	5.6590	179	80.00	3.5793
	0.6	246	68.26	4.9191	227	72.52	4.5392	136	84.80	2.7195
	0.8	193	75.10	3.8593	199	75.91	3.9793	84	90.61	1.6797
Root	Blank	775	-	15.4972	826	-	16.5170	895	-	17.8967
	0.2	374	51.75	6.4988	417	49.51	8.3385	213	76.20	4.2521
	0.4	356	54.06	5.5790	374	54.72	7.4786	198	77.88	3.9593
	0.6	343	55.74	4.9191	341	58.71	6.8187	147	83.58	2.9395
	0.8	255	67.10	3.8593	298	63.92	5.9589	89	90.06	1.7797

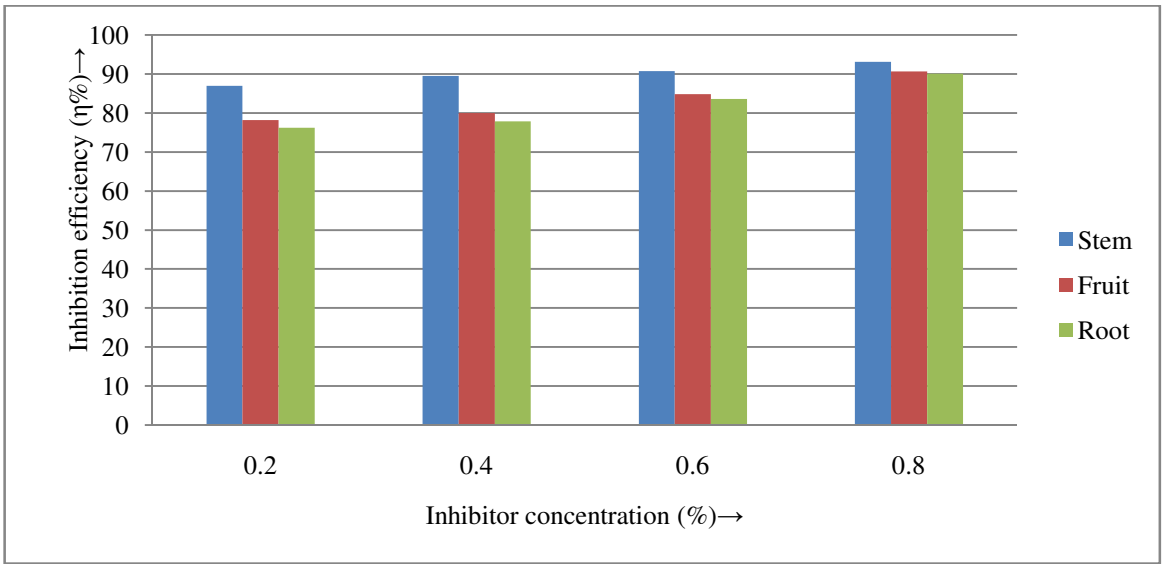
Table-2

Reaction Number (RN) and Inhibition efficiency (η %) for mild steel in HCl at 299±0.1 K with alcoholic extracts of plant *Leptadenia pyrotechnica*. (Area of exposure- 7.75 cm^2)

Plant part	Inhibitor concentration	3N HCl		2N HCl		1N HCl	
		(RN)	(η %)	(RN)	(η %)	(RN)	(η %)
Stem	Blank	0.1137	-	0.1005	-	0.0921	-
	0.2	0.0370	67.46	0.0352	64.98	0.0336	63.52
	0.4	0.0344	69.74	0.0321	68.06	0.0289	68.62
	0.6	0.0221	80.56	0.0223	77.81	0.0230	75.03
	0.8	0.0137	87.95	0.0149	85.17	0.0145	84.26
Fruit	Blank	0.1137	-	0.1005	-	0.0921	-
	0.2	0.0395	65.26	0.0376	62.59	0.0367	60.15
	0.4	0.0357	68.60	0.0367	63.48	0.0329	64.28
	0.6	0.0260	77.13	0.0273	72.84	0.0267	71.01
	0.8	0.0171	84.96	0.0177	82.39	0.0175	81.00
Root	Blank	0.1137	-	0.1005	-	0.0921	-
	0.2	0.0399	64.91	0.0396	60.60	0.0370	59.83
	0.4	0.0381	66.49	0.0369	63.28	0.0308	66.56
	0.6	0.0287	74.76	0.0301	70.05	0.0282	69.38
	0.8	0.0195	82.85	0.0183	81.79	0.0201	78.18

Table-3
Value of coefficient of correlation (r) between Inhibition efficiency (η %) and Inhibitor concentration of *Leptadenia pyrotechnica* for mild steel in 1.0 N HCl [Time- 24 hrs]

Plant part	Inhibitor concentration	Inhibition efficiency	X- $\bar{X}$	Y-$\bar{Y}$	$(dx)^2$	$(dy)^2$	dx x dy	r
Stem	0.2	63.83	-0.3	-9.925	0.09	98.5056	2.9775	0.9748
	0.4	72.53	-0.1	-1.225	0.01	1.5006	0.1225	
	0.6	77.85	0.1	4.095	0.01	16.7690	0.4095	
	0.8	80.81	0.3	7.055	0.09	49.7730	2.1165	
	$\bar{X}$ = 0.5	$\bar{Y}$= 73.755	∑X- $\bar{X}$=0	∑Y-$\bar{Y}$= 0	∑dx^2= 0.2	∑dy^2=166.5483	∑dx x dy =5.626	
Fruit	0.2	45.39	-0.3	-8.205	0.09	67.3220	2.4615	0.9984
	0.4	50.92	-0.1	-2.675	0.01	7.1556	0.2675	
	0.6	56.82	0.1	3.225	0.01	10.4006	0.3225	
	0.8	61.25	0.3	7.655	0.09	58.5990	2.2965	
	$\bar{X}$ = 0.5	$\bar{Y}$= 53.595	∑X- $\bar{X}$= 0	∑Y-$\bar{Y}$= 0	∑dx^2= 0.2	∑dy^2=143.4773	∑dx x dy =5.348	
Root	0.2	19.18	-0.3	-21.315	0.09	454.3292	6.3945	0.9885
	0.4	31.73	-0.1	-8.765	0.01	76.8252	0.8765	
	0.6	48.71	0.1	8.215	0.01	67.4862	0.8215	
	0.8	62.36	0.3	21.865	0.09	478.0782	6.5595	
	$\bar{X}$ = 0.5	$\bar{Y}$= 40.495	∑X- $\bar{X}$= 0	∑Y-$\bar{Y}$= 0	∑dx^2= 0.2	∑dy^2=1076.7189	∑dx xdy =14.652	



Figure–1
Variation of inhibition efficiency (η%) with inhibitor concentration (%) for mild steel in 1.5 N HCl of *Leptadenia pyrotechnica* (72 hrs)

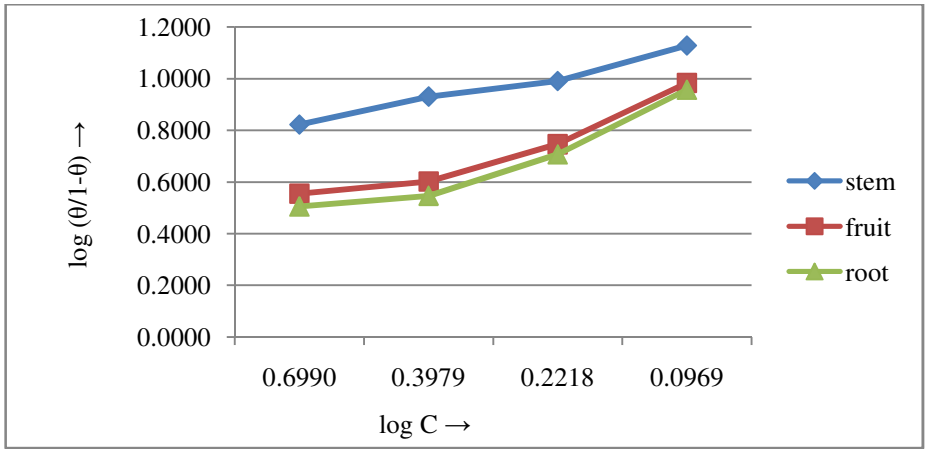


Figure – 2
Langmuir adsorption isotherm for mild steel in 1.5 N HCl with alcoholic extracts of *Leptadenia pyrotechnica* (72 hrs)

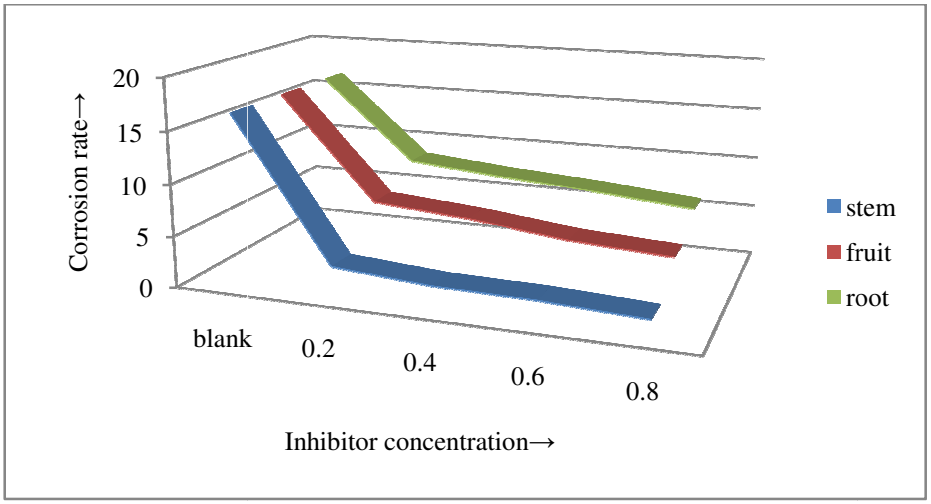


Figure- 3
Variation of corrosion rate with inhibitor concentration (%) of plant *Leptadenia pyrotechnica* for mild steel in 0.5N HCl

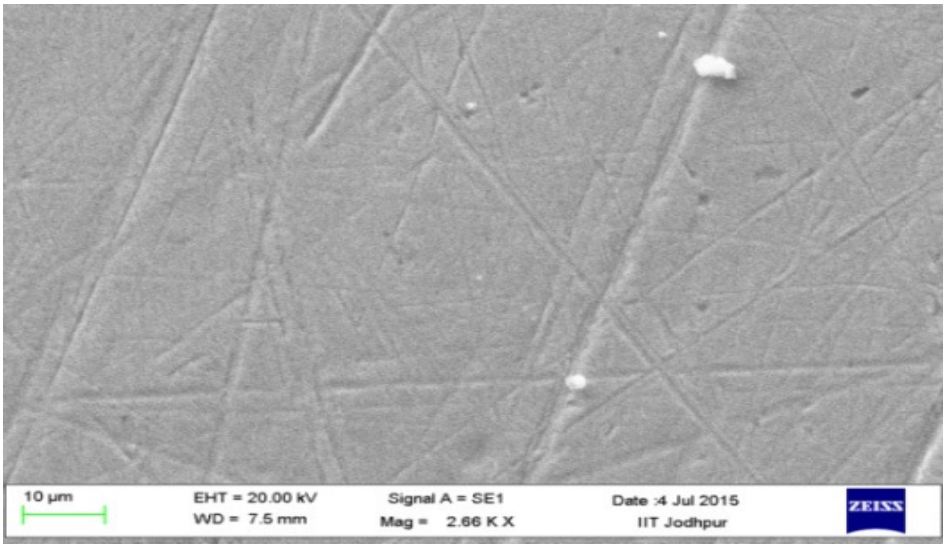


Figure- 4
SEM of pure mild steel

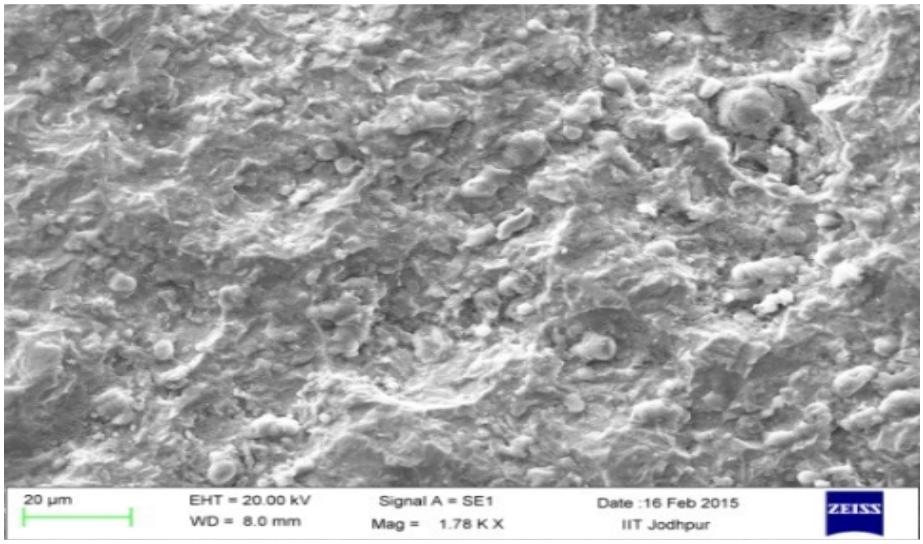


Figure- 5
SEM of mild steel in HCl

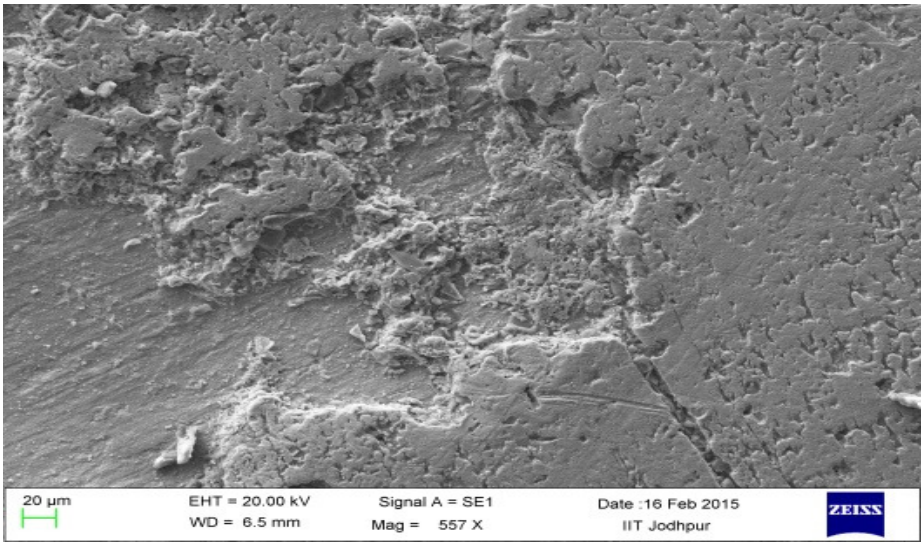


Figure- 6
SEM of mild steel in HCl with inhibitor (0.8%)

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