Inhibitive effect of alcoholic extract of *Pergularia daemia* on corrosion of mild steel in hydrochloric acid solution

Gajendra singh, S. K. Arora, S. P. Mathur, Renu Parashar

Abstract— **Green inhibitors are widely used due to their comparative advantage over other means of corrosion control and prevention. The inhibition efficiency of Pergularia daemia extract on the corrosion of mild steel in hydrochloric acid solution was measured by mass loss and thermometric method in the presence and in absence of inhibitor. It is concluded that the inhibition efficiency increased with the increase in inhibitor concentration. The investigation showed optimal inhibition efficiency up to 94.16% and can safely be used without pollution and any toxic effect.**

Index Terms— **Corrosion, Mild steel, Pergularia daemia, Weight loss method, Thermometric method, Correlation coefficient, Corrosion rate, Inhibition efficiency**

I. Introduction

Mild steel is widely used in engineering, automobile, boiler plates, pipes and in bridge and building work. Mild steel is used in various chemical industries due to its low cost, high strength and easy availability for fabrication of various reaction vessels, tank, pipes etc. Since it undergo severe corrosion attack in aggressive environment, it has to be protected. Acid solutions are often used in industries for cleaning, descaling and pickling of metallic structure. Corrosion is the deterioration of metal by chemical attack or reaction with its environment. Corrosion generally occurs at metal surface in the presence of oxygen and moisture. It is an electrochemical reaction. Oxidation takes place at anodic site and reduction occurs at cathodic site. It is a constant and continuous problem, often difficult to eliminate completely.

Corrosion inhibitors are organic or inorganic chemical compounds which are usually used in small concentration whenever a metal is in contact with an aggressive medium. Organic compounds having hetero atoms like N, O, and S and in some cases Se and P are found to have functioned as very effective corrosion inhibitor[1]. Over the year, considerable efforts have been deployed to find suitable corrosion inhibitor of organic origin in various corrosive media[2-5]. There are numerous naturally occurring substances like Heena[6], Tamarind, Tea leaves, Tannin, Beet-root[7], pomegranate juice and peel[8], Quinoline based cinchona alkaloids, Eucalyptus leaves extract[9] and very popular ayurvedic powder Mahasudarshana churna[10] have been reported as corrosion combating material. Corrosion inhibition efficiency of Eugenia jambolans[11], Adhatoda vasica, Prospis juliflora[12], Datura Stromonium[13], Curry leave[14], Brahmi[15], Hibiscus Cannabinus[16], Garlic[17], Ocimum sanctum[18], Cordia dichotoma[19] have also been reported. Recently the use of naturally occurring substances like Pennisetum glaucum[20], Molasses[21], Pumpkins[22], Black tea[23], Bhringaraj[24] and Araucaria columnaris[25] have been evaluated as effective green corrosion inhibitors.

In the present studies the inhibitive effects of alcoholic extract of stem, fruit and root of *Pergularia daemia* have been evaluated. Pergularia is a perennial twining herb, foul-smelling when bruised and with much milky juice, stem hairy. Leaves are opposite, membranous, 3-9 cm long and about as wide, broadly ovate, orbicular or deeply cordate, acute or short-acuminate at apex, pubescent beneath, petioles 2-9 cm long. Advantage of extract of *Pergularia daemia* as green inhibitor over the rest could be attributed to the following: it is easily available, cost effective, nontoxic, biodegradable and ecofriendly.

II. Experimental

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 Pergularia were obtained by drying, then finely powdered and extracted with boiling methanol. 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 efficacy was calculated as:

$$\text{Inhibition efficacy } (\eta\ \%) = \frac{100\,(\Delta M_u - \Delta M_i)}{\Delta M_u}$$

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

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

The corrosion rates in mmpy can be obtained by the following equation:

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

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 a thermal 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°C. Initially the increase in temperature was slow, then rapid, attaining a maximum value and then decreased. The maximum temperature was noted. The inhibition efficacy was calculated as

$$\text{Inhibition efficacy } (\eta\ \%) = \frac{100\,(RN_f - RN_i)}{RN_f}$$

Where RN_f and RN_i are the reaction number in the free solution and in inhibited solution respectively. Reaction number RN (K min^{-1}) is given as:

$$RN = \frac{T_m - T_i}{t}$$

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

Coefficient of Correlation

From mass loss data, coefficient of correlations (r) between the inhibitions additions and percentage inhibition efficacy can be calculated by using the formula-

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

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

III. Result and Discussion

Mass loss and inhibition efficiency for mild steel in various concentration of acid inhibitor are shown in table-1. It is observed that the inhibition efficiency increases with increase in the concentration of inhibitor and also increases with increase in acid strength. The corrosion rate decreases with increase in concentration of inhibitor. All the inhibitor has reduced the corrosion rate to a significant extent. Stem, fruit and root extract of *Pergularia daemia* exhibit maximum inhibition efficiency up to 94.17%, 92.05% and 90.60% respectively in 1.5 N HCl. The result reveals that inhibition efficiency increases with increase in inhibition concentration from 0.2% to 0.8%.

Inhibition efficiency was also determined using the thermometric method. Reaction numbers (RN) and inhibition efficiency in various concentrations of HCl (1N, 2N and 3N) are summarized in table- 2. The maximum inhibition efficiency obtained with the highest concentration (0.8%) of inhibitor and with the highest concentration of HCl (2.0N). The maximum inhibition efficacies observed by thermometric measurement are 89.89%, 86.81% and 85.49% for the stem, fruit and root respectively. The variation in reaction number (RN) with inhibitor concentration is depicted graphically in Fig.-2.

The value of correlation coefficient (r = 0.9845, 0.9548 and 0.9887) indicate that there is a high degree positive correlation between concentration and inhibition efficiency (η %), which proves that the inhibition efficacy increases with increase in the inhibitor concentration.

SEM Studies: Fig-5 shows the surface view of pure mild steel sample, Fig-6 is in 1.5N HCl after the exposure of mild steel sample for about 72 hours, whereas Fig- 7 is in 1.5N HCl with inhibitor (0.8%) for the same time. Fig.5 and 7 show almost same view of surface whereas Fig.6 shows immense roughness which depicts that the mild steel surface has been adversely affected in HCl. Corrosion has been almost combated by extract of *Pergularia daemia* which is indicated by almost same view of mild steel surface (Fig. 5 and 7).

Table – 1
Mass loss data for mild steel in HCl with alcoholic extracts of plant *Pergularia daemia* at 299 ± 0.1K
Area of exposure – 7.75cm²

	0.5N HCl (9 hrs)				1.0N HCl (24 hrs)			
Inhibitor Concentration (%)	Mass Loss (Δm) Mg	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)	Surface Coverage (θ)	Mass Loss (Δm) mg	Inhibition Efficiency (η %)	Corrosion Rate (mmpy)	Surface Coverage (θ)
Stem extract								
Blank	72		11.5179		223		13.3775	
.2	31	56.94	4.9591	0.5694	92	58.74	5.5190	0.5874
.4	22	69.44	3.5194	0.6944	79	64.57	4.7391	0.6457
.6	10	86.11	1.5997	0.8611	55	75.34	3.2994	0.7534
.8	5	93.06	0.7999	0.9306	24	89.24	1.4397	0.8924
Fruit extract								
Blank	72		11.5179		223		13.3775	

.2	48	33.33	7.6786	0.3333	101	54.71	6.0589	0.5471
.4	35	51.38	5.5990	0.5138	87	60.99	5.2190	0.6099
.6	16	77.78	2.5595	0.7778	69	69.06	4.1392	0.6906
.8	9	87.50	1.4397	0.8750	21	90.58	1.2598	0.9058
Root extract								
Blank	72		11.5179		223		13.3775	
.2	51	29.17	8.1585	0.2917	112	49.28	6.7188	0.4928
.4	37	48.61	5.9189	0.4861	94	57.85	5.6390	0.5785
.6	18	75.00	2.8795	0.7500	65	70.85	3.8993	0.7085
.8	13	81.94	2.0796	0.8194	28	87.44	1.6797	0.8744
	1.5N HCl (72 hrs)				2.0 N HCl (72 hrs)			
Stem extract								
Blank	755		15.0972		874		17.4768	
.2	189	74.96	3.7793	0.7496	175	79.88	3.4993	0.7988
.4	117	84.50	2.3396	0.8450	125	85.70	2.4995	0.8570
.6	99	86.89	1.9796	0.8689	112	87.19	2.2396	0.8719
.8	44	94.17	.8798	0.9417	83	90.50	1.6597	0.9050
Fruit extract								
Blank	755		15.0972		874		17.4768	
.2	197	73.91	3.9393	0.7391	197	77.46	3.9393	0.7746
.4	134	82.25	2.6795	0.8225	154	82.38	3.0794	0.8238
.6	112	85.17	2.2396	0.8517	131	85.01	2.6195	0.8501
.8	60	92.05	1.1998	0.9205	96	89.02	1.9196	0.8902
Root extract								
Blank	755		15.0972		874		17.4768	
.2	210	72.19	4.1992	0.7219	223	74.49	4.4592	0.7449
.4	164	78.28	3.2794	0.7828	189	78.38	3.7793	0.7838
.6	129	82.91	2.5795	0.8291	170	79.41	3.3994	0.7941
.8	71	90.60	1.4197	0.9060	128	85.55	2.5595	0.8555

Table- 2

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

Inhibitor concentration	3N HCl		2N HCl		1N HCl	
Stem extract	(RN)	(η %)	(RN)	(η %)	(RN)	(η %)
Blank	0.1137	-	0.1005	-	0.0921	-
.2	0.0348	69.39	0.0300	70.15	0.0302	67.21
.4	0.0262	76.96	0.0255	74.63	0.0253	72.53
.6	0.0197	82.67	0.0200	80.10	0.0196	78.72
.8	0.0115	89.89	0.0126	87.46	0.0138	85.02
Fruit extract						
Blank	0.1137	-	0.1005	-	0.0921	-
.2	0.0310	72.73	0.0318	68.36	0.0326	64.60
.4	0.0285	74.93	0.0246	75.52	0.0277	69.92
.6	0.0220	80.65	0.0211	79.00	0.0217	76.44
.8	0.0150	86.81	0.0148	85.27	0.0155	83.17
Root extract						
Blank	0.1137	-	0.1005	-	0.0921	-
.2	0.0374	67.11	0.0364	63.78	0.0365	60.37
.4	0.0279	75.46	0.0286	71.54	0.0287	68.84
.6	0.0213	81.27	0.0203	79.80	0.0215	76.66

.8	0.0165	85.49	0.0161	83.98	0.0174	81.11

Table-3

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

Inhibitor concentration	Inhibition efficacy	X- $\bar{X}$	Y-$\bar{Y}$	$(dx)^2$	$(dy)^2$	dx x dy
			Stem			
0.2	58.74	-0.3	-13.225	0.09	174.9006	3.9675
0.4	64.54	-0.1	-7.425	0.01	55.1306	0.7425
0.6	75.34	0.1	3.375	0.01	11.3906	0.3375
0.8	89.24	0.3	17.275	0.09	298.4256	5.1825
$\bar{X}$ =0.5	$\bar{Y}$=71.965	∑ X-$\bar{X}$=0	∑ Y-$\bar{Y}$=0	$\sum dx^2$=0.2	$\sum dy^2$=539.8475	∑ dx x dy =10.23
					r =0 .9845	
			Fruit			
0.2	54.71	-0.3	-14.125	0.09	199.5156	4.2375
0.4	60.99	-0.1	-7.845	0.01	61.5440	0.7845
0.6	69.06	0.1	0.225	0.01	0.0506	0.0225
0.8	90.58	0.3	21.745	0.09	472.8450	6.5235
$\bar{X}$ =0.5	$\bar{Y}$=68.835	∑ X-$\bar{X}$=0	∑ Y-$\bar{Y}$=0	$\sum dx^2$=0.2	$\sum dy^2$=733.9553	∑ dx x dy =11.568
					r = 0.9548	
			Root			
0.2	49.78	-0.3	-16.7	0.09	278.89	5.01
0.4	57.85	-0.1	-8.63	0.01	74.4769	0.863
0.6	70.85	0.1	4.37	0.01	19.0969	0.437
0.8	87.44	0.3	20.96	0.09	439.3216	6.288
$\bar{X}$ =0.5	$\bar{Y}$=66.48	∑ X-$\bar{X}$=0	∑ Y-$\bar{Y}$=0	$\sum dx^2$=0.2	$\sum dy^2$=811.7854	∑ dx x dy =12.598
			r =0 .9887			

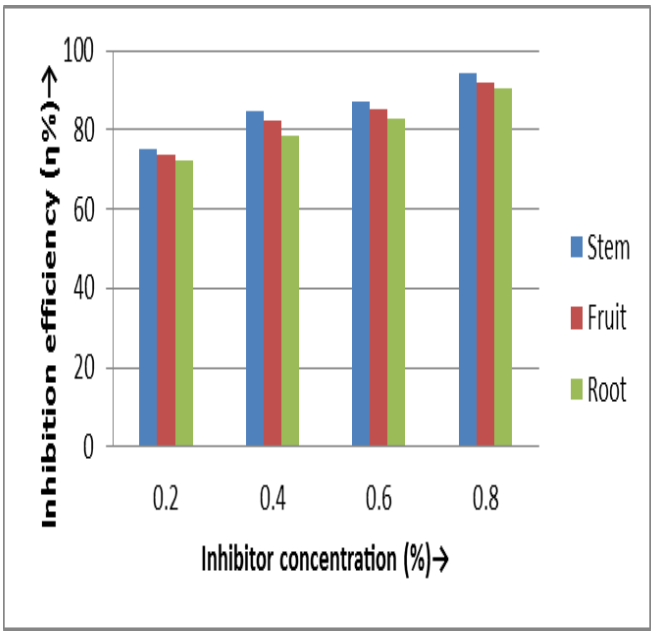

Figure – 1 variation of inhibition efficiency (η %) with inhibitor concentration (%) for mild steel in 1.5 N HCl of *Pergularia daemia* (72 hrs)

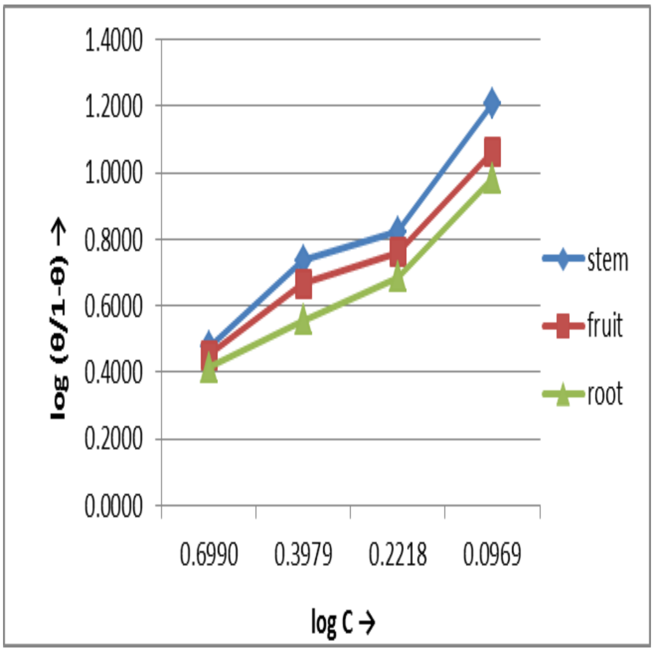

Figure – 2 Langmuir adsorption isotherm for mild steel in 1.5 N HCl with alcoholic extracts of *Pergularia daemia* (72hrs)

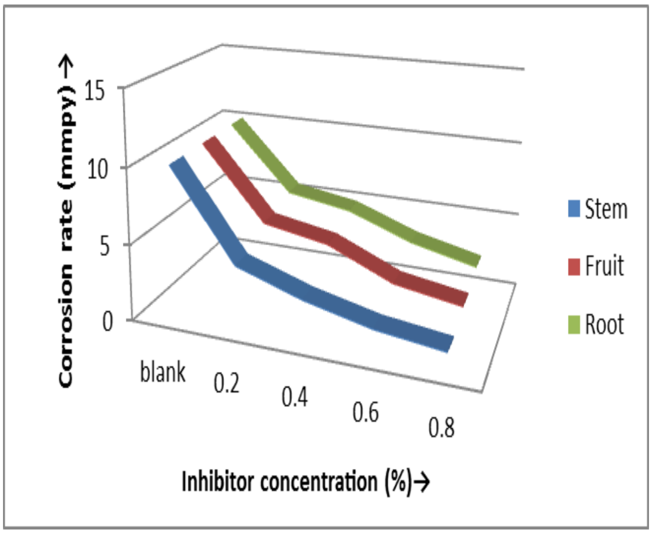

Figure- 3 Variation of corrosion rate with inhibitor concentration (%) of plant *Pergularia daemia* for mild steel in 0.5N HCl (24hrs)

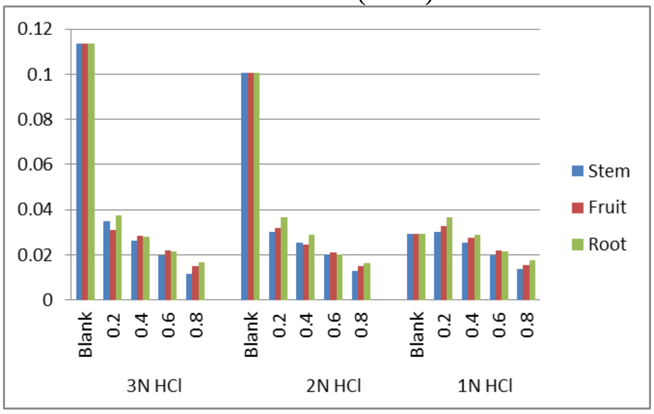

Figure – 4 Variation of reaction number with Inhibitor concentration for mild steel in 1.0 N HCl (24 hrs)

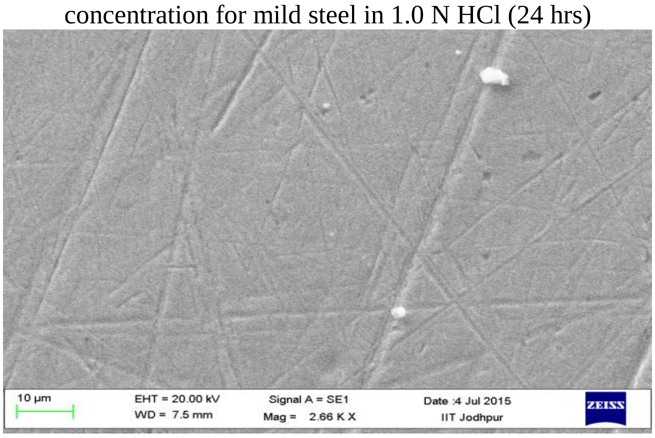

Fig.-5 SEM of pure mild steel

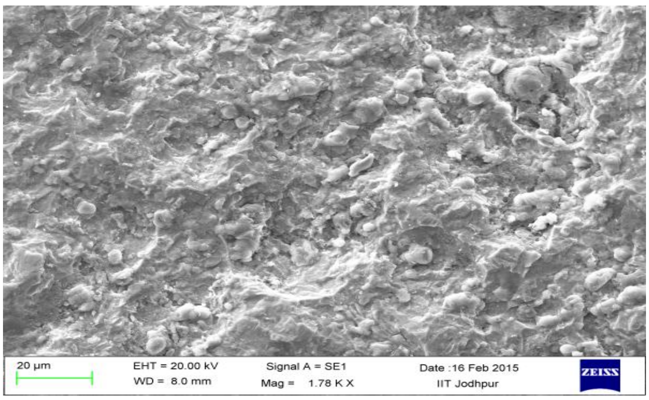

Fig.- 6 SEM of mild steel in 1.5N HCl

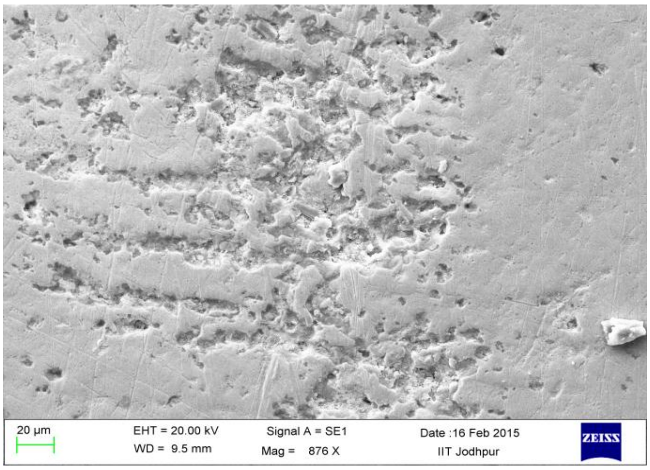

Fig.- 7 SEM of mild steel in 1.5N HCl with inhibitor (0.8%)

IV. Conclusions

The alcoholic extracts of *Pergularia daemia* are found to be effective inhibitor in acid media giving up to 94.17% efficiency and can safely be used without any corrosion damage, toxic effect and pollution.

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