Original Research Article
Annalen der chemischen Forschung
www.aocsr.com

Amaranthus extract as corrosion inhibitor for mild steel in pickling paste containing H_2SO_4

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Abstract

In the present work, the effect of *Amaranthus* extract as corrosion inhibitor for mild steel in pickling paste containing H_2SO_4 has been investigated. The weight loss experiments were conducted to bring forth results regarding various parameters, viz., concentration of inhibitor, concentration of acid, period of exposure, temperature, coating thickness and water content of paste. *Amaranthus* showed approximately 70% inhibition when the concentration of inhibitor changed from 0.5% to 5.0%.The inhibitive performance of *Amaranthus* improved with increase in concentration of H_2SO_4' with concentration ranging from 1N – 11N the inhibitor efficiency increased from 65% - 80%. The rate of attack on mild steel showed little variation with time of application. Percentage protection of inhibitor increased from 70% to 74% when coating thickness was increased from 1 gm/dm^2 to 5 gm/dm^2. *Amaranthus* maintained its good inhibitive performance over the entire range of temperature studied. The inhibitive performance of inhibitor decreased with decrease in water content.

Keywords : *Amaranthus* extract , mild steel, corrosion, inhibitor.

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1.0 Introduction

Iron and mild steel are used in large quantities for structural purposes and for fabrication of machine tools. Iron on exposure to moist air, is found to be covered with a reddish – brown coating called rust. The rust consists essentially of hydrated ferric oxide, $Fe_2O_3.3H_2O$, together with small quantity of ferrous carbonate, $FeCO_3$. Acid solutions are usually used for pickling in order to remove rust from their surface. Results indicate that metal dissolves most rapidly in pure sulfuric acid solution, somewhat more slowly in pure hydrochloric acid and slowest of all in pure phosphoric acid [1]. The dissolution of iron in H_2SO_4 is slowed down by halide ions [2].

$$\mathbf{Fe + 2HCl = FeCl_2 + H_2}$$

The hydrogen molecule, due to slow rate of formation in some cases, penetrates the crystal lattice and deforms it leading to brittleness of metal. Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by either chemisorption on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface [3].Because of the toxic nature and/or high cost of some chemicals currently in use as inhibitors, it is necessary to develop environmentally acceptable and inexpensive ones. Natural products can be considered as a good source for this purpose. The aqueous extracts from different parts of some plants such as Henna, *Lawsonia inermis* [4], Rosmarinous officinalis L. [5], *Carica papaya* [6], *cordia latifolia* and curcumin [7], date palm, *phoenix dactylifera*, henna, *lawsonia inermis*, corn, *Zea mays* [8], and *Nypa Fruticans Wurmb* [9] have been found to be good corrosion inhibitors for many metals and alloys. Leaves extracts are used as common corrosion inhibitors. The anticorrosion activity of Meethi neem (*Murraya koenigii)*, Amla (*Emblica officianilis*), Black Myrobalan (*Terminalia chebula*), soapberry (*Sapindus trifolianus*), and Shikakai (*Accacia conicianna*) was investigated. Corrosion inhibition has also been studied for the extracts of Beautiful swertia (*Swertia angustifolia*). Similar results were also shown by Eucalyptus (*Eucalyptus sp.*) leaves, Jambolan (*Eugenia jambolana*), sugar-apple (*Annona squamosa*), Babul (*Acacia Arabica*), Papaya (*Carica papaya*), Neem (*Azadirachta indica*) and Ironweed (*Vernonia amydalina*) were used for steel in acid media. Attap palm (*Nypa fructicans*) wurmb leaves were studied for the corrosion inhibition of mild steel in HCl media. Castor (*Ricimus communis*) leaves were studied for the corrosion inhibition of mild steel in acid media in addition to the use of herbs such as coriander, hibiscus, anis, black cumin, and garden cress as new type of green inhibitors for acidic corrosion of steel [10 - 15].Seeds are of great concern for corrosion inhibition studies. Tobacco (*Nicotiana*), black pepper (*Piper nigrum*), castor seeds oil (Ricinus communis), *acacia* gum, and lignin can be good inhibitors for steel in acid medium. *Papaya*, *Poinciana pulcherrima*, Fedegoso (*Cassia occidentalis*), and Datura (*Datura stramonmium*) seeds are efficient corrosion inhibitors for steel [16 - 18].

In the present work, our aim is to use inhibited pickling acid in the paste form so that it can be conveniently applied on large structures as well as on small tools to be pickled / cleaned. As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of *Amaranthus* extract, a green inhibitor which is commonly known as Pigweed.

2. .0 Materials and methods

Mild steel (Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr

0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135%) panels of size 10 cm X 7.5 cm of pickled cold rolled closed annealed mild steel (18 SWG) cut from a single sheet were used in all experiments. For identification of specimens all were numbered and a suspension hole of about 2 mm diameter near upper edge was made. The specimens were polished to mirror finish with emery paper. They were cleaned with cotton to remove powder and traces of adhered metal, and then they were degreased with sulfur – free toluene followed by cleaning with methanol before experiments. All the acid and chemicals used in the experiment were of AR grade quality.

Amaranthus

Distilled water was used for the preparation of solution. Clay – soil was collected, washed, dried, powdered and sieved. 100 gm sieved soil was taken in a plastic glass with a hole at the bottom. This glass was put over uninhibited and inhibited acids. Soil soaked acid uniformly and thus pickling paste was prepared. 100 gm soil soaked 31.3 cc acid. Polished and weighed panels were suspended by a V-shaped hook made of capillary over 100 % humidity for 6 months at room temperature. In 6 months, heavy rust appeared on the panels. Panels were re-weighed to get the amount of rust. Pickling paste was applied over weighed rusted panels under different conditions. After the experiment, paste was removed by washing with saturated sodium bicarbonate solution. The panels were again washed with water and dried with hot air. The panels were finally weighed to get the amount of rust dissolved. Experiments were conducted in triplicate and mean value is reported in the following tables.

The leaves of *Amaranthus* were crushed and squeezed. Liquid, thus obtained was used as inhibitor. 1 cc of extracted liquid was added to 100 cc of acid for the preparation of inhibited pickling paste.

The inhibitor efficiency was calculated from the following equation:

$$\% IE = [(Wu - W_i) / W_u] X 100$$

Where,

%IE = Inhibitor efficiency
W_u = Wt. loss without inhibitor
W_I = Wt. loss with inhibitor

Various variables which were studied are -concentration of inhibitor, concentration of acid, period of Exposure, temperature, coating thickness and water content of paste
.

3.0 Result and discussion

A. Effect of concentration of *Amaranthus* in H_2SO_4 :

The effect of concentration of *Amaranthus* (0.01% to 5.0%) in paste containing 4N H_2SO_4 on its inhibitive efficiency for mild steel at room temperature is shown in Table-1 and Figure-1(a & b). Results show that when 0.01% *Amaranthus* was added to paste, weight loss reduced from 27.9 mg/dm^2/hr to 10.8 mg/dm^2/hr, as the concentration of *Amaranthus* was further increased weight loss continuously decreased. At 5.0% concentration, the weight loss obtained was 7.8 mg/dm^2/hr. Inhibitor efficiency at 0.01% concentration of *Amaranthus* was 61% which continuously increased with increase in concentration of inhibitor upto 72% at 5.0% concentration
.

Concentration of inhibitor(%)	Weight loss(mg/dm^2)	Inhibitor Efficiency(%IE)
Nil	27.9	Nil
0.01	10.8	61
0.1	10.1	64
0.5	9.2	67
1	8.4	70
2	7.8	72
5	7.8	72

Table-1a: **Effect of concentration of inhibitor(*Amaranthus*)on the rate of attack of mild steel by paste [H_2SO_4(4N);RT;1 hr.;3.0 gm paste/dm^2 = coating thickness]**

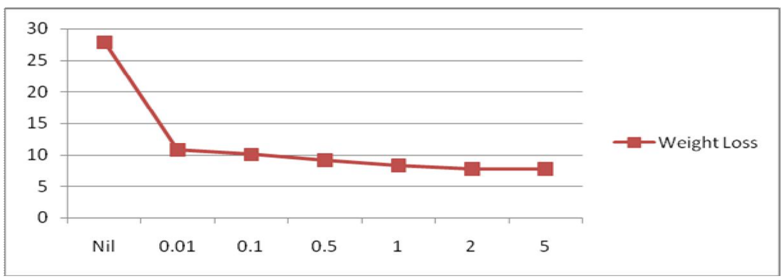

Figure-1b : **Effect of concentration of inhibitor(*Amaranthus*)on the rate of attack of mild steel by paste [H_2SO_4(4N);RT;1 hr.;3.0 gm paste/dm^2 = coating thickness]**
X axis : Concentration of inhibitor (%) , Y axis : weight loss(mg/dm^2)

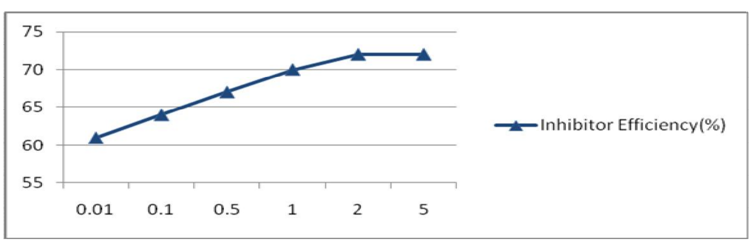

Figure-1b : **Effect of concentration of inhibitor (*Amaranthus*)on its inhibitive performance [H_2SO_4(4N);RT;1 hr.;3.0 gm paste/dm^2 = coating thickness]**
X axis : Concentration of inhibitor (%) , Y axis : inhibitor efficiency(%IE)

B. Effect of concentration of H_2SO_4

Table-2 and Figure-2(a & b) shows weight loss of mild steel in paste with different concentration of H_2SO_4 (1N – 11N) in the absence and presence of 1.0% *Amaranthus* at room temperature. Weight loss of mild steel specimens in paste with 1N to 11N H_2SO_4 varied from 21.3 mg/dm^2/hr to 59.1 mg/dm^2/hr; in inhibited system, weight loss obtained ranged from 7.5 mg/dm^2/hr to 11.8 mg/dm2/hr. The inhibitor efficiency varied from 65% to 80%.

Volume of acid (c.c)	Weight loss (mg/dm^2) Un.	In.	Inhibitor Efficiency (%IE)
1	21.3	7.5	65
2	23.6	7.3	69
3	24.7	7.9	68
4	27.9	8.4	70
5	29	7.8	73
7	38.4	9.9	74
9	46.2	10.6	77
11	59.1	11.8	80

Table-2 : Effect of change in concentration of H_2SO_4 in inhibited paste on the rate of attack of mild steel [RT;1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]

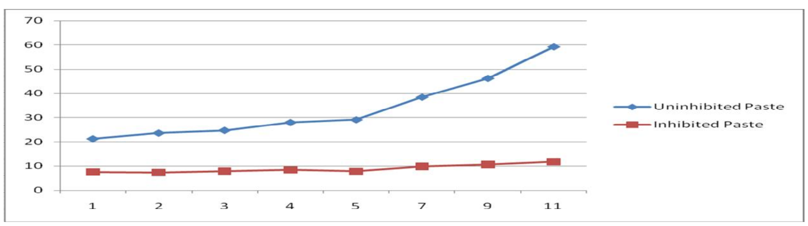

Figure- 2a : Effect of change in concentration of H_2SO_4 in paste on the rate of attack of mild steel [RT;1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Concentration of acid(N), Y axis : weight loss (mg/dm^2/hr)

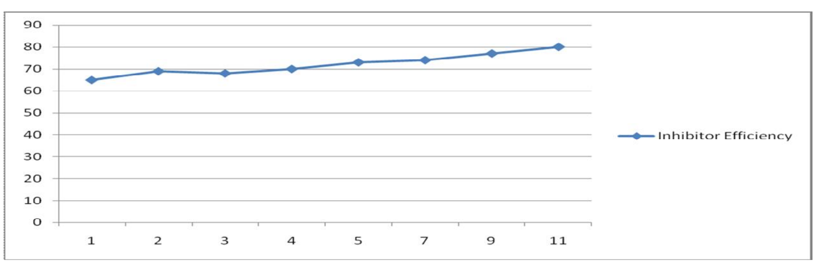

Figure- 2b : Effect of change in concentration of H_2SO_4 on efficiency of *Amaranthus* [RT;1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Concentration of acid(N), Y axis : Inhibitor efficiency (%IE)

C. Effect of time of application :

Table-3 and Figure-3(a & b) shows weight loss of mild steel specimens for 10 minutes to 180 minutes in uninhibited paste varied from 15.7 mg/dm^2 to 33 mg/dm^2 and in inhibited paste varied from 6.3 mg/dm^2 to 7.6 mg/dm^2. The inhibitor efficiency varied from 60% to 77%.

Time of Application (min.)	Weight loss (mg/dm^2)		Inhibitor Efficiency (%IE)
	Un.	In.	
10	15.7	6.3	60
30	21.1	6.8	68
60	27.2	7.6	72
120	30.9	7.7	75
180	33	7.6	77

Table-3 : Effect of time of application of paste on the rate of attack of mild steel[H_2SO_4(4N);RT;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]

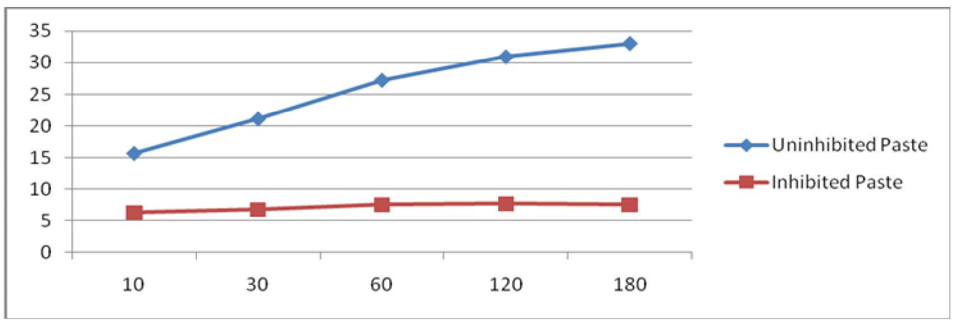

Figure-3a : Effect of time of application of paste on the rate of attack of mild steel[H_2SO_4(4N);RT;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Time of application (min.)
Y axis : weight loss (mg/dm^2)

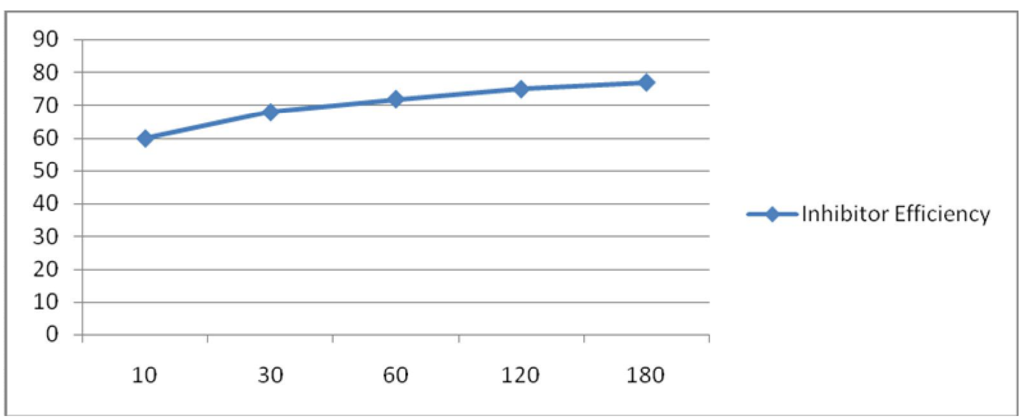

Figure-3b : Effect of time of application of paste on the inhibitive performance of *Amaranthus*[H_2SO_4(4N);RT;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Time of application (min.), Y axis : Inhibitor Efficiency (%IE)

D. Effect of temperature :
Table-4 and Figure-4(a & b) show the effect of temperature (30°C-60°C) on attack of mild steel due to paste containing 4N H_2SO_4 with and without 1.0% *Amaranthus*. In uninhibited paste, the weight loss of mild steel specimens varied from 23.1 $mg/dm^2/hr$ to 51.2 $mg/dm^2/hr$ in a temperature range of 30°C to 60°C. In inhibited paste, the weight loss varied from 6.2 $mg/dm^2/hr$ to 11.2 $mg/dm^2/hr$. The inhibitor efficiency varied from 73% at

30°C to 78% at 60°C. Arrhenius plots have been drawn showing the dependence of log corrosion rate on 1/T for uninhibited paste and inhibited paste. The linear nature of both the curves indicates that they obey the Arrhenius Equation.

Temperature (°C)	$1/T * 10^4$	Weight loss (mg/dm^2)				Inhibitor Efficiency (%IE)
		Un.	log Weight loss	In.	log Weight loss	
30	33	23.1	1.3636	6.2	0.7924	73
35	32.4	26.9	1.4298	7.3	0.8633	73
40	31.9	29.3	1.4669	7.6	0.8808	74
45	31.4	32.7	1.5145	8.8	0.9345	73
50	30.9	37.4	1.5729	9.3	0.9685	75
55	30.4	44.8	1.6513	10.7	1.0294	76
60	30	51.2	1.7093	11.2	1.0492	78

Table-4 : Effect of Temperature on the rate of attack of mild steel [H_2SO_4 (4N);1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%] (Also shows the values of 1/T and log weight loss to obtain Arrhenius plot)

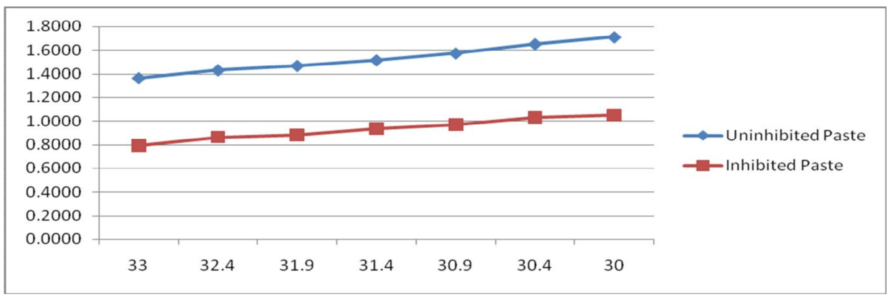

Figure-4a : Effect of Temperature on the rate of attack of mild steel [H_2SO_4 (4N);1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%] [Arrhenius Plot]
X axis : 1/T * 104, Y axis : log weight loss

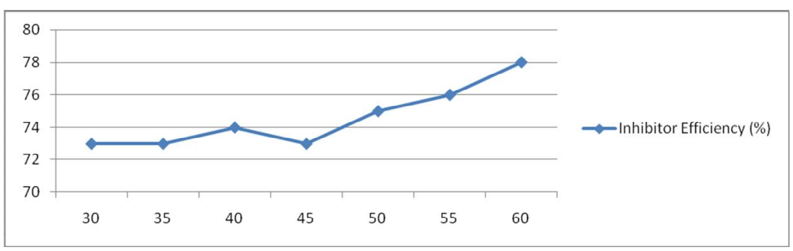

Figure-4b : Effect of Temperature on inhibitive performance of *Amaranthus* [H_2SO_4 (4N);1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Temperature (°C), Y axis : Inhibitive Efficiency (%IE)

E. Coating Thickness :

Effect of coating thickness(1 gm/dm^2 to 5 gm/gm^2) on the attack of mild steel in paste containing 4N H2SO4 with and without 1% *Amaranthus* at room temperature is shown in Table-5 and Figure-5(a & b). Results show that weight loss of mild steel specimens having paste (uninhibited) thickness 1 gm/ dm^2 to 5 gm/ dm^2 varied from 18.3 mg/ dm^2 to 31.5 mg/dm^2; in inhibited paste the weight loss ranged between 5.5 mg/dm^2 to 8.3 mg/ dm^2. Inhibitor efficiency changed from 70% to 74%.

Coating Thickness (gm/dm^2)	Weight loss (mg/ dm^2)		Inhibitor Efficiency (%)
	Uninhibited	Inhibited	
1	18.3	5.5	70
2	23	6.7	71
3	28.1	7.6	73
4	29.7	8	73
5	31.5	8.2	74

Table-5 : Effect of Coating thickness of inhibited paste on the rate of attack of mild steel[H_2SO_4 (4N);RT;1 hr.; *Amaranthus* = 1%]

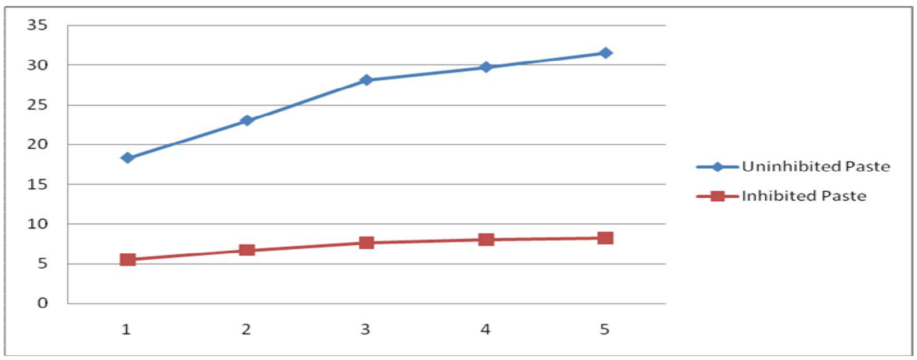

Figure-5a : Effect of Coating thickness on the rate of attack of mild steel[H_2SO_4 (4N);1 hr.; RT; *Amaranthus* = 1%]
X axis : Coating Thickness (gm/dm^2), Y axis : Weight loss (mg/ dm^2)

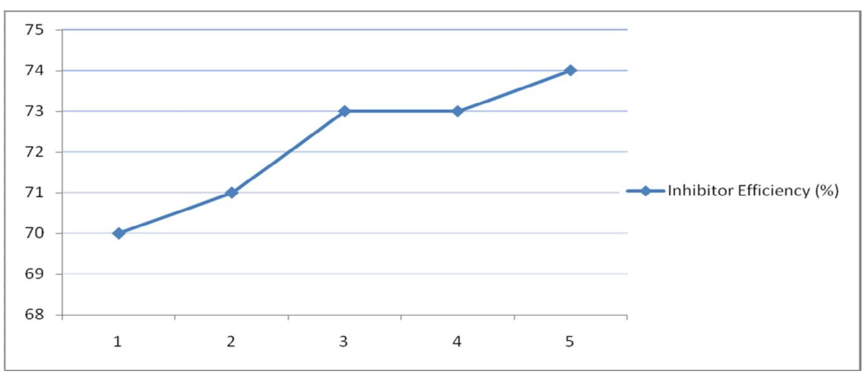

Figure-5b : Effect of Coating thickness on the inhibitor efficiency of *Amaranthus*[H_2SO_4 (4N);1 hr.; RT; *Amaranthus* = 1%]
X axis : Coating Thickness (gm/dm^2), Y axis : Inhibitive Efficiency (%IE)

F. Water content of paste
Table-6 and Figure-6(a & b) show the effect of water content (100% - 50%) of paste on the inhibition of corrosion of mild steel by1.0% *Amaranthus* (paste containing 4N H2SO4). Results show that in uninhibited paste, weight loss of mild steel specimens varied from 27.1 mg/dm2/hr to 28.3 mg/dm2/hr in the range of 100% water to 50% water. In inhibited

paste, the weight loss varied from 7.3 mg/dm2/hr to 9.6 mg/dm2/hr for the same range of water content. It is seen that the decrease in water content does not hamper the effectiveness of the inhibitor. The inhibitor efficiency varied from 73% at 100% water content to 66% at 50% water content.

Water Content (%)	Weight loss (mg/dm^2)		Inhibitor Efficiency (%)
	Un.	In.	
100	27.1	7.3	73
90	27.7	7.8	72
80	28.9	8.4	71
70	31.2	9	71
60	29.6	9.2	69
50	28.3	9.6	66

Table-6: Effect of water content of inhibited paste on the rate of attack of mild steel[H_2SO_4 (4N);RT;1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]

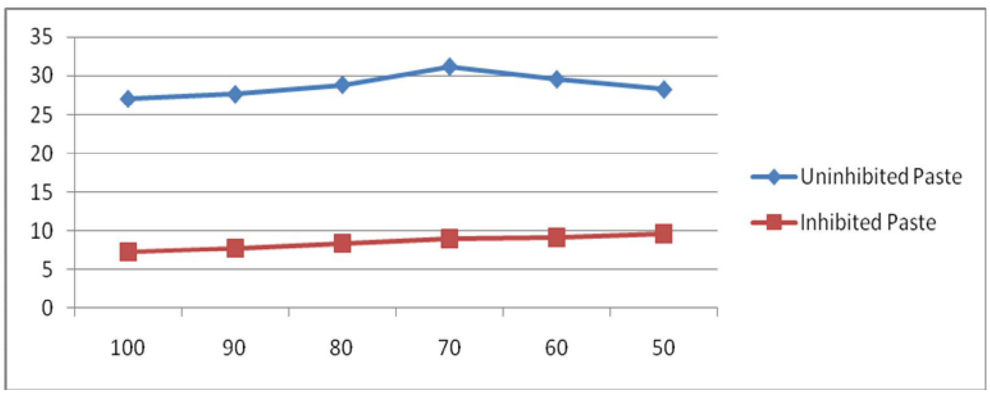

Figure -6a : Effect of water content on the rate of attack of mild steel[H_2SO_4 (4N);RT; 1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Water Content(%), Y axis : Weight loss (mg/ dm^2/hr)

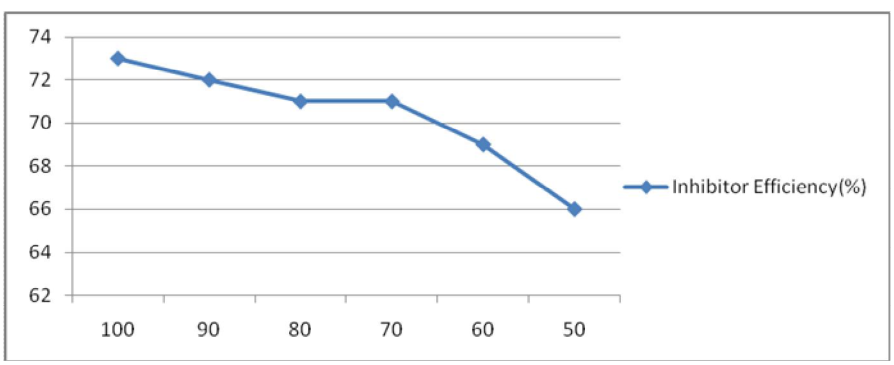

Figure-6b : Effect of water content on the inhibitor efficiency of *Amaranthus*[H_2SO_4 (4N);1 hr.;3.0 gm paste/dm^2 = coating thickness; *Amaranthus* = 1%]
X axis : Water Content(%), Y axis : Inhibitive Efficiency (%IE)

4.0 Conclusion

Results from the present study showed that *Amaranthus* *e*xtract has excellent inhibition properties for the corrosion of mild steel in 4N H2SO4 solution. The adsorption of *Amaranthus* leaves extract is uniform over the surface. The inhibition is due to the formation of the film on the metal/acid solution interface through adsorption of *Amaranthus* leaves extract molecules.

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