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Corrosion Inhibition and Electro-ballistic properties of Green Inhibitor for Mild Steel in Mineral Acid

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ABSTRACT

Implementation of *Amaranthus* extract as corrosion inhibitor for mild steel in pickling containing hydrochloric acid has been investigated. The electrochemical experiments were conducted to bring forth results regarding various parameters, viz., Corrosion Current, Anodic Polarization and Cathodic Polarization. Alongside, experiments for assessing the inhibitor efficiency and concentration of acid were also conducted. There was observed a gradual decrease in corrosion current with time for both uninhibited and inhibited systems. The experiments for plotting polarization curves for mild steel at various concentrations of *Amaranthus* extract in aerated solutions were conducted. These experiments, which are conducted Galvano-statically, depicted the polarization effect of inhibitor on different electrodes. The values, thus obtained, indicated that adsorption of *Amaranthus* extract tends to modify the mechanism of anodic dissolution as well as cathodic hydrogen evolution. The results clearly show that both the cathodic and anodic reactions are inhibited and there was found an increase in inhibition as the inhibitor concentration increases in acid media, but the cathode was more polarized than anode. This indicated that *Amaranthus* extract may be classified as cathodic inhibitor in 4N hydrochloric acid solution. The aim of conducting these experiments is to use inhibited acid for pickling so that large structures as well as small tools can be pickled/ cleaned. As a contribution to the current interest on environment friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of *Amaranthus* extract, a green inhibitor which is commonly known as Pigweed.

Key words : Amaranthus *extract, Mild steel, Corrosion, Inhibitor, Polarization.*

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 (Putilova, 1960). The dissolution of iron in H_2SO_4 is slowed down by halide ions (Srivastava and Sanyal, 1970).

$Fe + 2HCl = FeCl_2 + H_2$

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 (Srivastava and Srivastava, 1981).

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* (Al-Sehaibani, 2000), *Rosmarinous officinalis* L. (Kliškiæ *et al.*, 2000), *Carica papaya* (Okafor and Ebenso, 2007), *cordia latifolia* and curcumin (Farooki *et al.*, 1999), date palm, *phoenix dactylifera*, henna, *lawsonia inermis*, corn, *Zea mays* (Rehan, 2003), and *Nypa Fruticans Wurmb* (Orubite and Ofork, 2004) 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 (Noor, 2008; Buchweishaija and Mhinzi, 2008; Oguzie, 2008; Okafor *et al.*, 2008; Quraishi *et al.*, 2010; Noor, 2009). 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*), Datura (*Datura stramonmium*) seeds are efficient corrosion inhibitors for steel (de Souza and Spinelli, 2009; Badiea and Mohana, 2009; Chauhan and Gunasekaran, 2007), Terminalia Catappa Leaves extract (Madu1, 2019; Sukirno and Nasikin, 2018), Melia azedarach leaves extract (Ali and Mahrous, 2017), Thymus vulgaris plant extract (Ehsan *et al.*, 2017).

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

Experimental

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 * 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. Distilled water was used for the preparation of solution. 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 reweighed to get the amount of rust.

Weighed rusted panels were exposed for pickling 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 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 solution.

The inhibitor efficiency was calculated from the following equation:

$$\%IE = \frac{W_u - W_i}{W_u} \times 100$$

Where,

% IE = Percentage Inhibitor efficiency

W_u = Wt. loss without inhibitor

W_i = Wt. loss with inhibitor

Corrosion current was measured using ammeters of ma range by making galvanic couples of mild steel and platinum. Mild steel and platinum couple was put in acid solution (inhibited and uninhibited), they were connected through ammeter to record the corrosion current flowing through couple. Corrosion current as a function of time was measured.

Polarization measurements were made using following instruments

1. Transistorized current source (CV/CC 30 V-/ A with voltmeter and ammeter)
2. Equitronics Digital Potentiometer 4 ½ Digit
3. Equitronics Digital Current Meter
4. Decade Resistance Box
5. Saturated Calomel Electrode

Current was supplied from power source through available resistance. Current was measured using a multimeter. The electrochemical studies were made using a three-electrode cell assembly at room temperature. The mild steel was the working electrode, platinum electrode was used as an auxiliary electrode, and standard calomel electrode (SCE) was used as reference electrode. The working electrode was polished with different grades of emery papers, washed with water, and degreased with acetone. All electrochemical measurements were carried out using Potentio-stat / Galvano-stat.

Variables Studied

1. Concentration of inhibitor
2. Concentration of acid
3. Corrosion Current
4. Polarization (Anodic and Cathodic)

Result and Discussion

Effect of concentration of inhibitor in acid

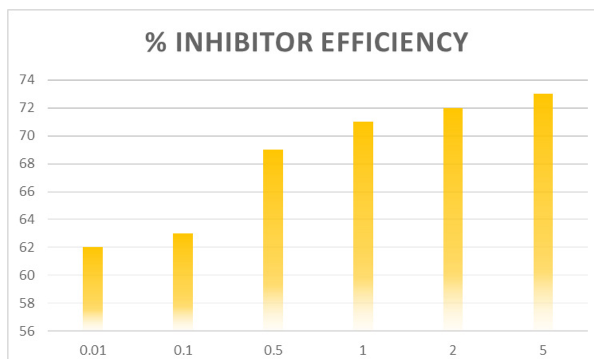
The effect of concentration of inhibitor 0.01% to 5.0% on its inhibitive efficiency for mild steel in solution containing 4N HCl at room temperature is shown in Table 1 and Figure 1[a and b]. Results show that when 0.01% *Amaranthus* was added to acid, weight loss reduced from 27.7 mg/dm^2/hr to 10.6 mg/dm^2/hr, as the concentration of inhibitor was further increased, weight loss continuously decreased. At 5% concentration, the weight loss obtained was 7.8 mg/dm^2/hr. Inhibitor efficiency was 62% which continuously increased with increase in concentration of inhibitor up to 73%.

Table 1. Effect of concentration of inhibitor (*Amaranthus*) on the rate of attack of mild steel [HCl(4N);1 hr.]

Concentration of inhibitor (%)	Weight loss (mg/dm^2)	Inhibitor Efficiency(%IE)
Nil	27.7	Nil
0.01	10.6	62
0.1	10.2	63
0.5	9.5	69
1	8.3	71
2	7.7	72
5	7.8	73

X axis: Concentration of inhibitor (%) **Y axis**: weight loss (mg/dm^2)

Fig. 1a. Effect of concentration of inhibitor (Amaranthus) on the rate of attack of mild steel [HCl(4N); 1 hr.]



X axis: Concentration of inhibitor (%)
Y axis: inhibitor efficiency(%IE)

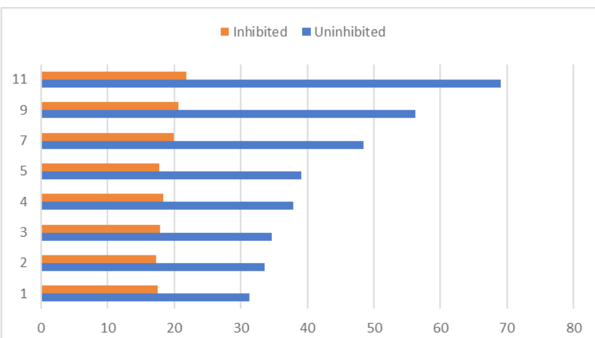
Fig. 1b. Effect of concentration of inhibitor (Amaranthus) on the rate of attack of mild steel [HCl(4N); 1 hr.]

Effect of Concentration of acid

Table 2 and Figure 2 [a and b] shows rate of dissolution of rust and weight loss of mild steel with different concentration of HCI [1N- 11N] in the absence and presence of 1.0% *Amaranthus* at room temperature the addition of inhibitor reduced the weight loss considerably, weight loss of mild steel specimens with 1N to11N HCI varied from 31.3 mg/ dm^2/hr to 69.1 mg/dm^2/hr ; in inhibited system weight loss obtained ranged from 17.5 mg/dm^2/hr to 21.8 mg/dm^2/hr. The inhibitor efficiency ranged from 65% in 1N to 80% in 11N HCl.

Table 2. Effect of change of concentration of HCl on the rate of attack of mild steel [RT; 1 hr.; *Amaranthus* = 1%]

Concentration of acid (N)	Weight loss (mg/dm^2)		Inhibitor Efficiency (%IE)
	Un.	In.	
1	31.3	17.5	65
2	33.6	17.3	69
3	34.7	17.9	68
4	37.9	18.4	70
5	39.1	17.8	73
7	48.4	19.9	74
9	56.2	20.6	77
11	69.1	21.8	80

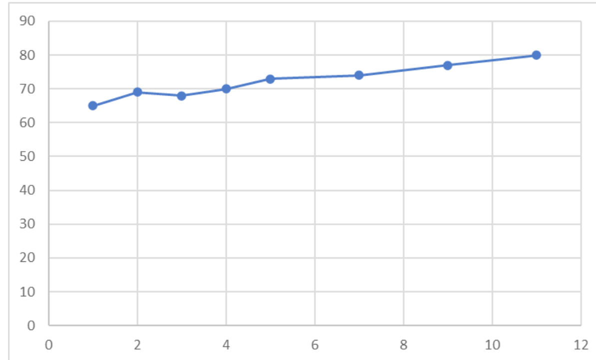


X axis: Concentration of inhibitor (%)
Y axis: inhibitor efficiency(%IE)

Fig. 2a. Effect of change of concentration of HCl on the rate of attack of mild steel [RT; 1 hr.; *Amaranthus* = 1%]

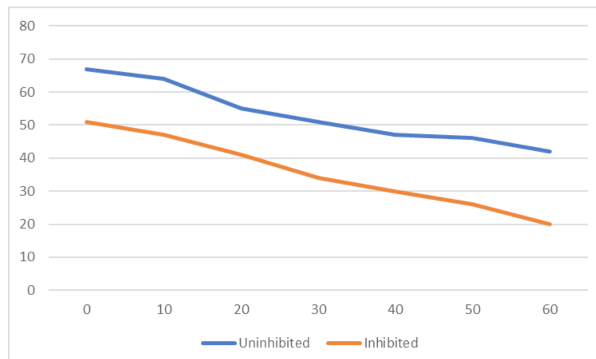
Table 1. Corrosion Current in steel platinum couple placed in paste [4N HCl; RT; *Amaranthus* = 1%]

Time (min.)	Current (ma)	
	Uninhibited	Inhibited
0	67	51
10	64	47
20	55	41
30	51	34
40	47	30
50	46	26
60	42	20



X axis: Concentration of acid(N) **Y axis**: weight loss (mg/dm^2/ hr)

Fig. 2b. Effect of change of concentration of HCl on inhibitor efficiency of *Amaranthus* [RT; 1 hr; *Amaranthus* = 1%]



X axis: Time (min) **Y axis**: Current (ma)

Fig. 1. Corrosion Current in steel platinum couple placed in paste [4N HCl; RT; Amaranthus = 1%]

Corrosion Current as a function of time for mild steel-platinum couple

Mild steel was connected to platinum and both were placed in 4N HCl with and without 1.0% *Amaranthus*. Results given in Table 1 and Figure 1 show that in uninhibited system, when steel was connected to platinum, the starting current was 67 ma. The current gradually decreased with time. In inhibited system, the starting current was 51 ma which gradually reduced to 20 ma.

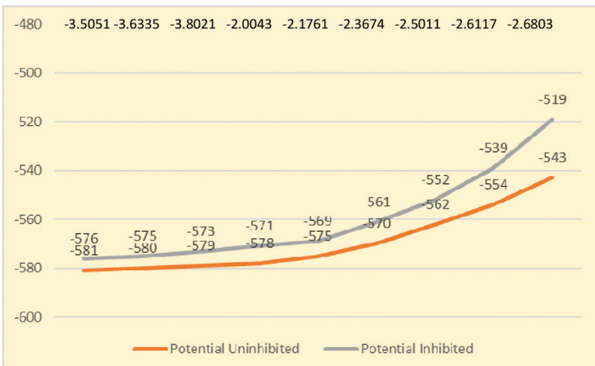
Polarization for mild steel

Anodic Polarization

Table 2 and figure 2 shows anodic polarization data for mild steel exposed to 4N HCl with and without 1.0% *Amaranthus*. Results show that when current was raised from 3.2*10^{-3} ma to 47.8*10^{-3} ma, the potential increased from -581 mV to -543 mV for uninhibited system. In inhibited system, the potential varied from -576 mV to -519 mV. Thus, *Amaranthus* polarized anode to some extent.

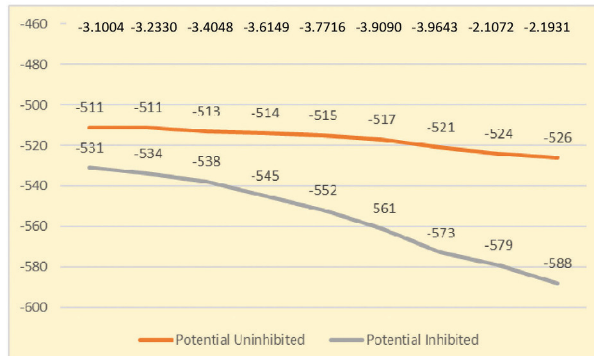
Cathodic Polarization

Table 3 and figure 3 show cathodic polarization data for mild steel exposed to 4N HCl with and without 1.0% *Amaranthus*. Results show a potential drop when current was raised from 1.2*10^{-3} ma to 15.6*10^{-3} ma for uninhibited system. For inhibited system, at minimum current density (1.2*10^{-3} ma/cm^2) potential was -531 mV which decreased to -588 mV at maximum current density (15.6*10^{-3} ma/ cm^2). Thus, a potential drop, ÄV of 57 mV was observed suggesting that *Amaranthus* polarized cathode to a considerable extent.



X axis: log current density **Y axis**: Potential (mV vs SCE)

Fig. 2. Anodic Polarization data for mild steel placed in paste [RT; 4N HCl; *Amaranthus* = 1%]



X axis: log current density **Y axis**: Potential (mV vs SCE)

Fig. 3. Cathodic Polarization data for mild steel [RT; 4N H_2SO_4; *Amaranthus* = 1%]

Table 2. Anodic Polarization data for mild steel [RT; 4N HCl; *Amaranthus* = 1%]

Current Density (ma/cm^2)	log CD	Potential Uninhibited (mV vs SCE)	Potential Inhibited (mV vs SCE)
3.2 * 10^{-3}	-3.5051	-581	-576
4.3 * 10^{-3}	-3.6335	-580	-575
6.4 * 10^{-3}	-3.8021	-579	-573
10.1 * 10^{-3}	-2.0043	-578	-571
15.0 * 10^{-3}	-2.1761	-575	-569
23.3 * 10^{-3}	-2.3674	-570	-561
31.7 * 10^{-3}	-2.5011	-562	-552
40.9 * 10^{-3}	-2.6117	-554	-539
47.8 * 10^{-3}	-2.6803	-543	-519

Table 3. Cathodic Polarization data for mild steel [RT; 4N HCl; *Amaranthus* = 1%]

Current Density (ma / cm^2)	log CD	Potential Un. (mV vs SCE)	Potential In (mV vs SCE)
1.2 * 10^{-3}	-3.1004	-511	-531
1.7* 10^{-3}	-3.233	-511	-534
2.5* 10^{-3}	-3.4048	-513	-538
4.1* 10^{-3}	-3.6149	-514	-545
5.9* 10^{-3}	-3.7716	-515	-552
8.1* 10^{-3}	-3.909	-517	-561
9.2* 10^{-3}	-3.9643	-521	-573
12.8* 10^{-3}	-2.1072	-524	-579
15.6* 10^{-3}	-2.1931	-526	-588

Conclusion

All measurements showed that *Amaranthus* extract has excellent inhibition properties for the corrosion of mild steel in 4N HCl 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. *Amaranthus* polarizes cathode and thus acts as a Cathodic Inhibitor.

Declaration of Conflicting Interests

The author declares no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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