

Electrochemical Properties of Green Inhibitor for Mild Steel in Pickling Paste Containing H_2SO_4



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Abstract

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, $Fe_2O_3 \cdot 3H_2O$, together with small quantity of ferrous carbonate; $FeCO_3$. Acid solutions are usually used for pickling in order to remove rust from their surface. Inhibitors prove to be of great importance as they curb the further loss of metal.

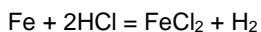
Implementation of *Amaranthus* extract as corrosion inhibitor for mild steel in pickling paste containing H_2SO_4 has been investigated. The electrochemical experiments were conducted to bring forth results regarding various parameters, viz., Corrosion Current, Anodic Polarisation and Cathodic Polarisation. 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 Potentiostat / Galvanostat. Corrosion Current was measured using ammeters of ma range by making galvanic couples of mild steel and platinum.

The corrosion current gradually decreased with time for both uninhibited and inhibited systems. Polarization curves for mild steel at various concentration of *Amaranthus* extract in aerated solutions were conducted. These experiments which are conducted galvanostatically show the polarization effect of inhibitor on different electrodes. The values indicate that adsorption of *Amaranthus* extract modifies the mechanism of anodic dissolution as well as cathodic hydrogen evolution. From the results, it is clear that both the cathodic and anodic reactions are inhibited and the inhibition increases as the inhibitor conc. increases in acid media, but the cathode is more polarized. This result indicated that *Amaranthus* extract can be classified as cathodic inhibitor in 4N H_2SO_4 solution. Thus, by conducting these experiments 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.

Keywords: *Amaranthus* Extract, Mild Steel, Corrosion, Inhibitor, Polarisation.

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, $Fe_2O_3 \cdot 3H_2O$, 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].



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], Rosmarinus 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 Wurbm* [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 (*Emblca 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 amygdalina*) were used for steel in acid media. Attap palm (*Nypa fruticans*) 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 stramonium)* seeds are efficient corrosion inhibitors for steel [16 - 18].

Aim of the Study

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.



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.

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 Table.

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.

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 pickling paste (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. Steel was used as working electrode and platinum foil as auxiliary electrode.

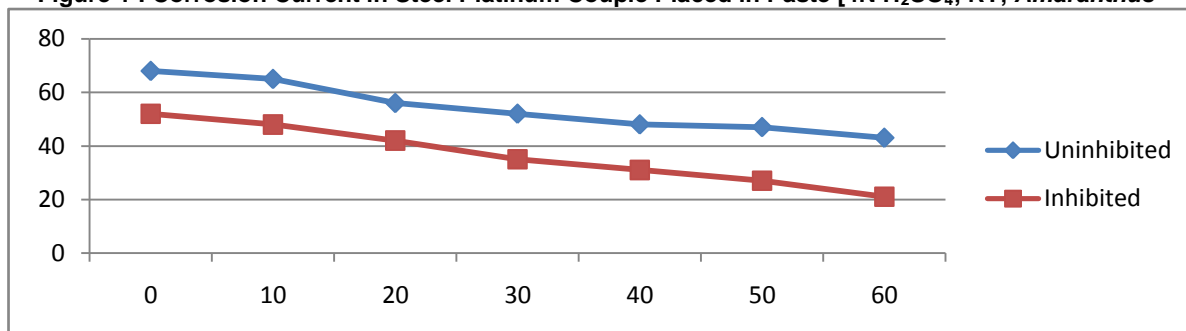
Variables Studied

1. Corrosion Current

Table 1: Corrosion Current in Steel Platinum Couple Placed in Paste [4N H₂SO₄; RT; *Amaranthus* = 1%]

Time (min.)	Current (ma)	
	Uninhibited	Inhibited
0	68	52
10	65	48
20	56	42
30	52	35
40	48	31
50	47	27
60	43	21

Figure 1 : Corrosion Current in Steel Platinum Couple Placed in Paste [4N H₂SO₄; RT; *Amaranthus* = 1%]



X axis : Time (min)

Y axis : Current (ma)

Polarization for Mild Steel

Anodic Polarization

Table 2 and figure 2 shows anodic polarization data for mild steel exposed to pickling paste containing 4N H₂SO₄ with and without 1.0% *Amaranthus*. Results show that when current was

2. Polarization (Anodic & Cathodic)

Result and Discussion

Corrosion Current as a Function of Time for Mild Steel-Platinum Couple

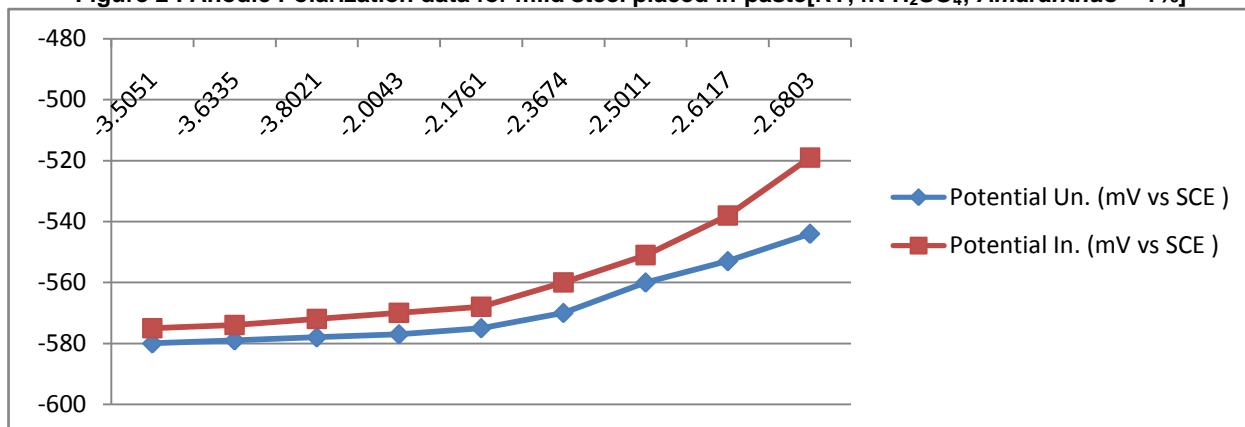
Pickling paste with 4N H₂SO₄ with and without 1.0% *Amaranthus* was prepared. Mild steel was connected to platinum and both were placed in pickling paste. Results given in table 1 and figure 1 show that in uninhibited system, when steel was connected to platinum, the starting current was 68 ma. The current gradually decreased with time. In inhibited system, the starting current was 52 ma which gradually reduced to 21 ma.

raised from 3.2*10⁻³ ma to 47.8*10⁻³ ma the potential increased from -580 mV to -544 mV for uninhibited system. In inhibited system, the potential varied from -575 mV to -519 mV. Thus, *Amaranthus* polarized anode to some extent.

Table 2 : Anodic Polarization data for mild steel placed in paste[RT; 4N H₂SO₄ ; *Amaranthus* = 1%]

Current Density (ma/cm ²)	log CD	Potential Uninhibited (mVvsSCE)	Potential Inhibited (mVvsSCE)
3.2 * 10 ⁻³	-3.5051	-580	-575
4.3 * 10 ⁻³	-3.6335	-579	-574
6.4 * 10 ⁻³	-3.8021	-578	-572
10.1 * 10 ⁻³	-2.0043	-577	-570
15.0 * 10 ⁻³	-2.1761	-575	-568
23.3 * 10 ⁻³	-2.3674	-570	-560
31.7 * 10 ⁻³	-2.5011	-560	-551
40.9 * 10 ⁻³	-2.6117	-553	-538
47.8 * 10 ⁻³	-2.6803	-544	-519

Figure 2 : Anodic Polarization data for mild steel placed in paste[RT;4N H₂SO₄; Amaranthus = 1%]



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

Cathodic Polarization

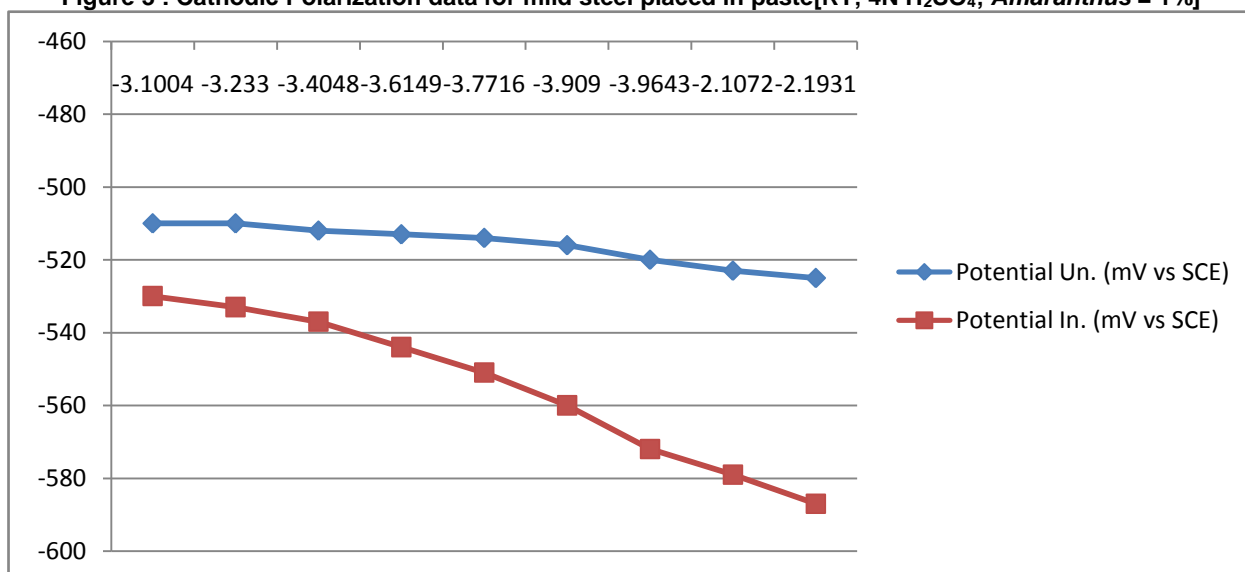
Table 3 and figure 3 show cathodic polarization data for mild steel exposed to pickling paste containing 4N H₂SO₄ with and without 1.0% *Amaranthus*. Results show a potential drop when current was raised from 1.2*10⁻³ ma to 15.6*10⁻³ ma for uninhibited system. For inhibited system, at

minimum current density (1.2*10⁻³ ma/cm²) potential was -530 mV which decreased to -587 mV at maximum current density (15.6*10⁻³ ma/cm²). Thus, a potential drop, ΔV of 57 mV was observed suggesting that *Amaranthus* polarized cathode to a considerable extent.

Table 3 : Cathodic Polarization data for mild steel placed in paste[RT; 4N H₂SO₄ ; 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	-510	-530
1.7 * 10 ⁻³	-3.233	-510	-533
2.5 * 10 ⁻³	-3.4048	-512	-537
4.1 * 10 ⁻³	-3.6149	-513	-544
5.9 * 10 ⁻³	-3.7716	-514	-551
8.1 * 10 ⁻³	-3.909	-516	-560
9.2 * 10 ⁻³	-3.9643	-520	-572
12.8 * 10 ⁻³	-2.1072	-523	-579
15.6 * 10 ⁻³	-2.1931	-525	-587

Figure 3 : Cathodic Polarization data for mild steel placed in paste[RT; 4N H₂SO₄; Amaranthus = 1%]



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

Conclusion

All measurements showed that *Amaranthus* extract 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. *Amaranthus* polarizes cathode and thus acts as a Cathodic Inhibitor.

Endnotes

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