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# Corrosion inhibition in mild steel by anodizing and the extract of Emblica Officinalis

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**ABSTRACT**

**Purpose:** Corrosion is the process of degradation of the materials due to its interaction with the atmosphere. All materials are susceptible to corrosion. Among all other materials metals are the most widely used materials. Metals are widely used for their properties such as high strength, ductility, thermal resistance and formability. So it is important to establish suitable methods to inhibit the corrosion of such materials. In this paper the material mild steel has been selected as it is one of the most commonly used material. The method used for corrosion inhibition is anodization followed by sealing using an ecofriendly corrosion inhibitor. The eco-friendly material that is tested in this paper is Emblica officinalis more commonly called as Amla. The material is first anodized in a 50% NaOH solution at elevated temperatures and their corresponding corrosion inhibition is studied using weight loss method. Properties such as adhesion, heat resistance are also tested for the material. FTIR is used to identify the coating produced by anodizing and also for the identification of the functional bonds in the ecofriendly corrosion inhibitor.

**Keywords:** Mild steel corrosion inhibition; NaOH anodization; Eco-friendly corrosion inhibitor

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**MANUFACTURING AND PROCESSING**

## 1. Introduction

Corrosion is a natural process, which converts refined metal to their more stable oxide. By this the gradual destruction of materials (usually metals) takes place by continuous chemical reaction with their environment. In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen [1-6]. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal, and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers. Corrosion in such materials is generally termed as degradation. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Corrosion is a major problem in all engineering applications. According to a study conducted at USA $276 billion is lost due to corrosion alone. Corrosion not only causes reduction of the life time of a product but also increases safety risks. Many structures and pipelines have failed leading to major accidents and loss of life. So it is important to reduce corrosion as much as possible. Among all the metals that are affected by corrosion mild steel is one that is most affected [1-9]. Mild steel is widely used for its low cost and good physical and mechanical characteristics such as tensile strength. If mild steel is exposed to an aerated neutral aqueous solution, for example a dilute solution of sodium chloride in water, then corrosive attack will begin at defects in the oxide film on the steel. These defects may be present as a result of mechanical damage such as scratches, or may be due to natural discontinuities in the film, i.e. inclusions, grain boundaries or dislocation networks at the surface of the steel.

The proposed work is to optimize this process and to study the characteristics of the coating. The mild steel will be analysed by conducting various test (Weight loss method for hydrochloric acid and sulphuric acid, sodium chloride solution, Scanning Electron Microscopy, potentiometric study and FTIR Spectroscopy). The magnetite coated mild steel will again be coated with amla extract and analysis will be conducted to compare the corrosion inhibition with the corroded mild steel.

## 2. Experiments conducted

Mild steel C1018 coupons were used in this investigation. The coupons had the composition (in wt%) of 0.18% C, 0.02% Cr, 0.03% Cu, 0.79% Mn, 0.02% Ni, 0.022% P, 0.024% S, 0.21% Si and balance is iron. The were cut to the dimensions 5 cm x 4 cm x 1.2 mm. A hole is punched on the corner of the plate to aid in suspending the sample into the anodizing solution. These samples were cleaned of the surface impurities and oxides using sand paper, degreased using acetone followed by immersion for two minutes in 10% HCl to activate the surface.

### 2.1. Preparation of the experimental setup

The setup consists of a voltage and current controlled power supply generally called as a regulated power supply (RPS). A one litre beaker filled with NaOH solution at 50% concentration will act as the container in which the anodizing will take place. The beaker is placed on a magnetic stirrer and hot plate apparatus (Fig. 1). The stirrer with hot plate is used to eliminate the need for two separate equipment. The solution is stirred to ensure the dissipation of the bubbles formed during the process. If the bubbles formed are not dissipated the formation of the coating is greatly retarded. The hot plate is used to increase the temperature of the setup to the required value. Since the temperature cannot be reliably maintained using just the hot plate the temperature of the solution is measured externally using a thermometer.

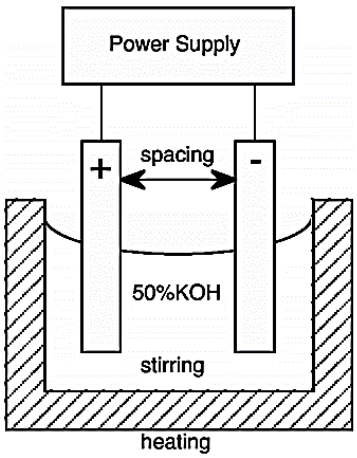


Fig. 1. Schematic representation of experimental setup

Two sample plates are dipped into the solution with a distance of 5 cm as inferred from literature review. Care should be taken to ensure that the samples do not touch each other or there may be a short circuit. By varying the voltage in the equipment and the hot plate temperature the samples are anodized for 20 minutes. The coating is formed on the positive plate by the diffusion of iron into hot sodium hydroxide solution. The samples should be allowed to stand in the hot solution to allow it to attain equilibrium temperature. The sample is retrieved and rinsed with distilled water to remove any sodium hydroxide residue.

### 2.2. Emblica officinalis extract

Emblica officinalis leaves were washed with distilled water and dried in shade for 5 days. Then it was powered with the help of a mixer. 5 grams of the fine powder was mixed with distilled water and refluxed for 8 hours. The

Five different concentrations (200 ppm, 400 ppm, 600 ppm, 800 ppm and 1000 ppm) of the extract were prepared for the corrosion study by weight loss method in hydrochloric acid, sulphuric acid and sodium chloride solutions. The anodized mild steel samples were used for the tests after thoroughly washed with acetone and distilled water. The samples were immersed in the solution for 24 hours at atmospheric conditions. The specimens were removed washed with water and dried. The mass of the specimens before and after immersion was determined using an electronic digital balance.

### 2.3. Weight loss method

Weight loss method is used to estimate the corrosion by measuring the difference in the weights before and after the corrosion has taken place. The mild steel strips were cut into pieces are pickled in pickling solution (1% $H_2SO_4$) for 3 minutes and washed with distilled water. After drying, the steel plates were polished with various grades of emery papers and degreased using acetone. Three surface cleaned substrate was weighed and one strip was taken as reference, other samples were coated with the oxide layer. Each strip weight was noted after drying and immersed in 0.1 N HCl, $H_2S0_4$ and NaCl solution for 24 hours at room temperature in different beakers. After 24 hours the strips were taken out from the beakers and dried in room temperature then the weight of the each strips were noted. The corrosion rate was calculated by weight loss method using the following equation.

Corrosion rate =

$$\text{(Weight loss x 87.6)/(Density x Area x time)} \quad (1)$$

Similarly, inhibition efficiency was calculated using the equation,

$$IE\% = (CR0\text{-}CR1/\ CR0)\ \text{x}100 \quad (2)$$

where,
IE % = Inhibition Efficiency

CR0 and CR1 are the values of the Corrosion rate (mmpy) of mild steel and paint coated mild steel respectively.

## 3. Results and discussion

The anodization of mild steel is carried out in a 50% concentrated hot sodium hydroxide solution. This concentrated solution was prepared by mixing 500 grams of sodium hydroxide in one litre of distilled water. The polished mild steel anode and cathode were placed in the solution such that they don't touch each other. The factors that influence the anodization of the mild steel are temperature of the bath, voltage applied and distance between the plates. The distance of 5 cm is maintained a constant throughout this experiment. The temperature and voltage are varied to identify the effect of these parameters in the anodization of the mild steel samples. In order to establish the range within which the coating can be formed without compromising the quality the Anodizing was carried out at different voltages varying from 0 to 4 volts. It was observed that at voltages greater than 3.5 volts defects in the coating were formed due to the bubbles generated during the process. So from the literature review and the tests conducted a voltage range of 2.5 volts to 3.5 volts was found to be the range in which the required blue black adherent layer was formed with sufficient quality (without uncoated areas due to the bubble generation).

The solution was prepared by dissolving 500 grams of NaOH in 1 litre water. Before anodization the solution was clear in nature. Once the current is passed through the solution the solution turns dark violet indicating the dissolution of iron into the solution from the electrode. All the samples were anodized using the same solution. After a few hours the solution turns green and the iron present in its +3 oxidation state lowers to its +2 oxidation state and forms sediments to the bottom of the solution. The solution can be reused after the removal of the iron sediments from the solution. This can be achieved by simple filtration.

The sample is made to undergo various tests to determine the nature of the coating. The test used are SEM analysis, adhesion testing by cross cut tape test, heat resistance test and FTIR spectroscopy.

The SEM analysis shows that the coating is formed over the plain mild steel but the surface is porous and will prove to be a good surface for the coating to adhere to (Fig. 2).

### 3.1. Adhesion test

The main aim of this test is to test the adhesion of the coating. The most important property of a coating is adhesion. The higher the adhesion the greater is the corrosion inhibition. Select an area free of blemishes and minor surface imperfections. Under the illumination of the magnifier, use the cross-cut tool to make parallel cuts and test the surface for its adhesion. The adhesion test was done according to ASTM D3359 standard. The coating has very good adhesion and a rating ASTM class 5B rating was obtained. This shows that the coating is highly adherent and can withstand adverse conditions.

(a)

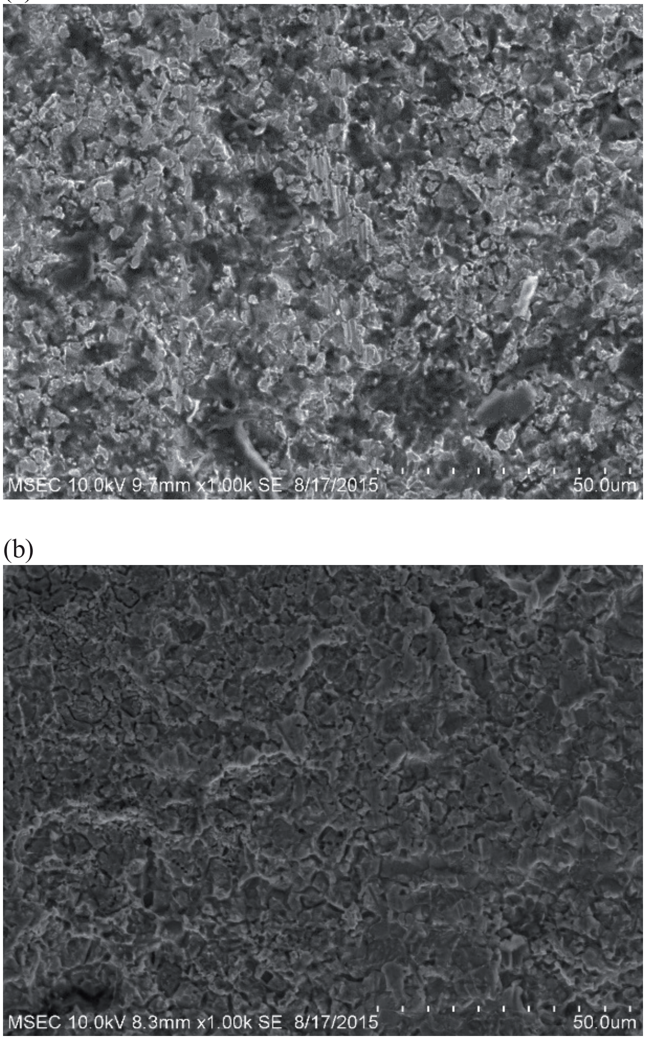


Fig. 2. SEM images of (a) plain mild steel and (b) anodized mild steel

## 3.2. Heat resistance test

The ability of the coating to withstand high temperatures was tested. The sample was kept for 24 hours in a muffle furnace at 500°C and then retested the results showed that there was no significant change in the characteristics of the material. This shows the resistance of the coating to heat.

## 3.3. FTIR analysis

The sample was subjected to FTIR to characterize the coating material as magnetite. The occurrence of peaks in the region between 530 $cm^{-1}$ and 600 $cm^{-1}$ proves the presence of magnetite ($Fe_3O_4$) in the coating (Fig. 3).

## 3.4. Weight loss method

Corrosion inhibition properties of various coatings have been evaluated by dipping the painted film in various mineral acids 0.1N HCl, $H_2S0_4$ and NaCl solution respectively. Before testing the corrosion inhibition property of various coating, the corrosion rate of the test specimen (mild steel) has been evaluated by dipping plain steel in the acid for about 24 hours. After that, the changes in weight of the steel specimen were noted down. The samples are dipped in the solution prepared at 0.1 normality for 100 ml for 24 hours. After which it is weighed and the corrosion rate and inhibition efficiency of the samples are calculated. The values are summarized in the Tables 1-6.

From the obtained results it is clear that the anodized mild steel has some corrosion resistance of its own, but it is necessary to conduct a process called sealing for any anodization process which generally employs a synthetic coating. It would be better to use an organic corrosion inhibitor in the place of the synthetic one as organic inhibitors are better than synthetic in cost, manufacturing methodology and ecofriendly nature. So I have chosen the leaf and stem extract of emblica officinalis to be used as the natural inhibitor. Thus it is important to test the corrosion characteristics of the extract with the anodized mild steel.

The extract prepared is made to undergo FTIR test to identify the functional bonds which are known to provide corrosion inhibition in the extract (Fig. 4). The peaks obtained at 1027.13 denotes C-N bond and the peaks 1716.80, 1158.51, 1314.11 and 1205.41 denote C-O bond, similarly peaks at 1604.09 denote N-H, 2848.63 and 2916.68 denote O-H stretch and 596.73 denote C-Br stretch. Nitrogen and oxygen bonds are essential for the inhibitive nature of the materials.

The anodized mild steel sample with the highest inhibition towards corrosion is taken. These samples are tested with emblica officinalis against different mediums. These tests will help identify the compatibility of the emblica officinalis extract towards the $Fe_3O_4$ layer formed on the anodized mild steel.

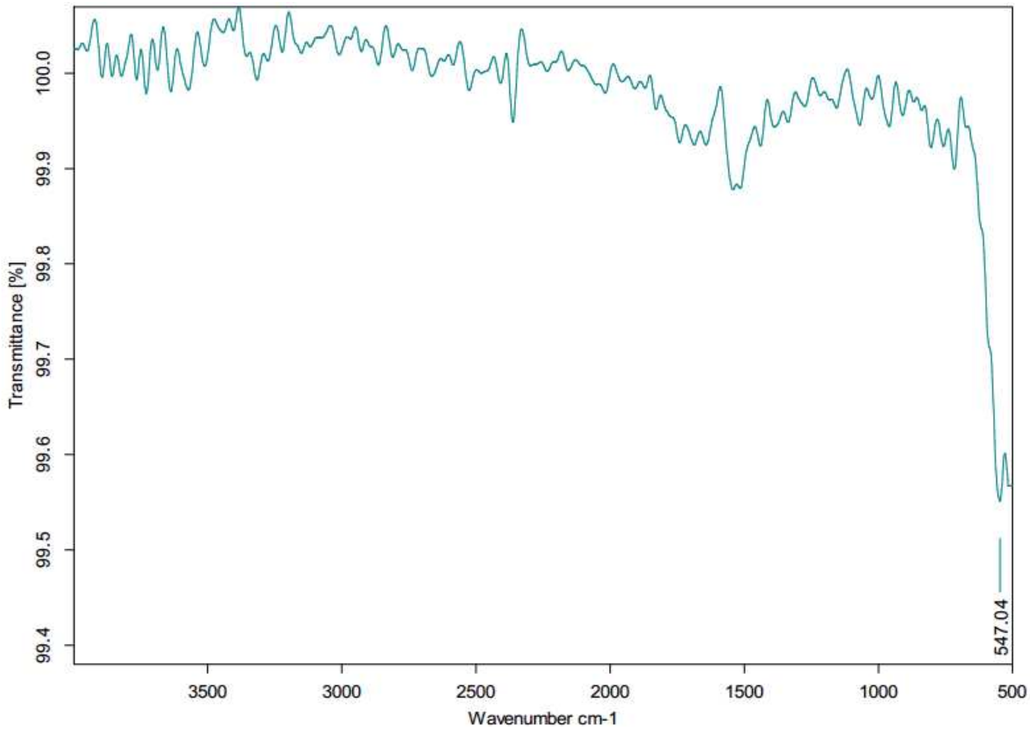


Fig. 3. FTIR of the anodized mild steel

Table 1.
Corrosion behavior of plain and coated steel in HCl medium

| Coated specimen | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| Plain steel | 25.985 | 25.577 | 0.4082 | 0.949 | - |
| Coated Steel 1 | 24.309 | 24.148 | 0.1611 | 0.3745 | 60.53 |
| Coated Steel 2 | 25.846 | 25.695 | 0.1512 | 0.3515 | 62.95 |
| Coated Steel 3 | 24.703 | 24.566 | 0.1368 | 0.318 | 66.48 |
| Coated Steel 4 | 25.477 | 25.317 | 0.1598 | 0.3715 | 60.8 |
| Coated Steel 5 | 24.585 | 24.438 | 0.1474 | 0.3426 | 63.89 |
| Coated Steel 6 | 25.346 | 25.213 | 0.1322 | 0.3073 | 67.61 |

Table 2.
Corrosion behavior of plain and coated steel in $H_2SO_4$ medium

| Coated specimen | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| Plain steel | 24.5832 | 23.3622 | 1.2210 | 2.838 | – |
| Coated Steel 1 | 24.4115 | 24.0765 | 0.3350 | 0.779 | 72.55 |
| Coated Steel 2 | 25.8336 | 25.5222 | 0.3114 | 0.724 | 74.49 |
| Coated Steel 3 | 24.6398 | 24.3757 | 0.2641 | 0.614 | 78.36 |
| Coated Steel 4 | 25.4278 | 25.1005 | 0.3273 | 0.761 | 73.19 |
| Coated Steel 5 | 26.4935 | 26.1877 | 0.3058 | 0.711 | 74.95 |
| Coated Steel 6 | 26.8343 | 26.5776 | 0.2567 | 0.594 | 78.96 |

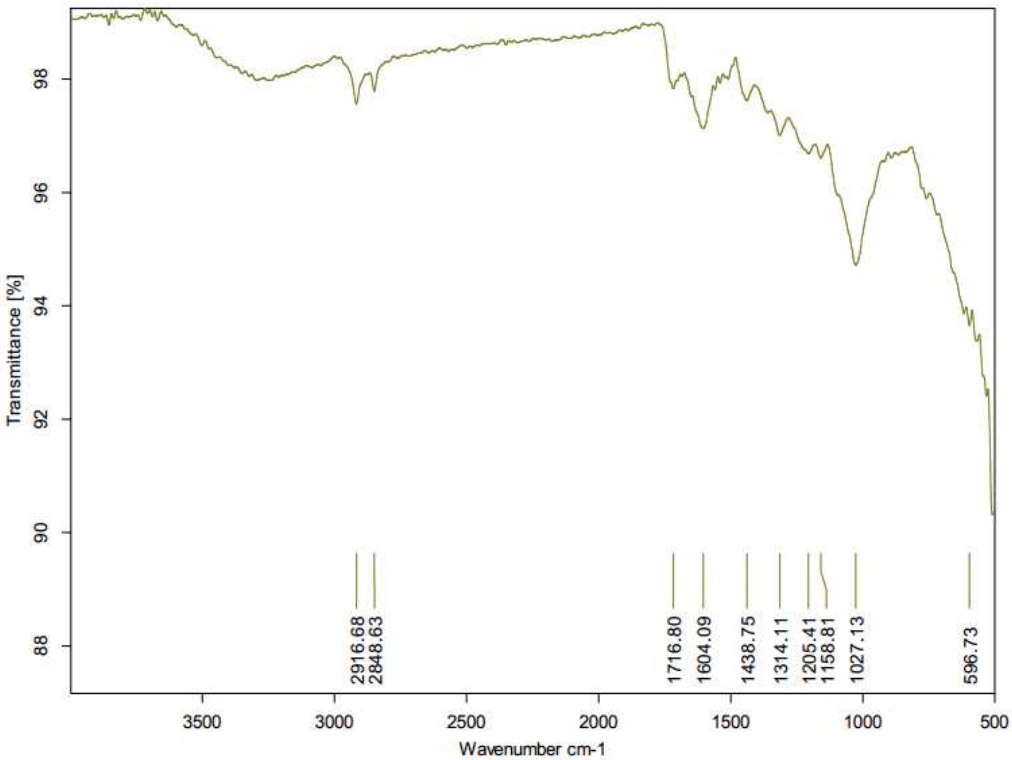


Fig. 4. FTIR spectroscopy for Emblica officinalis extract

Table 3.
Corrosion behaviour of plain and coated steel in NaCl medium

| Coated specimen | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| Plain steel | 25.6961 | 25.4576 | 0.2385 | 0.5544 | - |
| Coated Steel 1 | 25.5767 | 25.5259 | 0.0508 | 0.1182 | 78.6 |
| Coated Steel 2 | 25.1477 | 25.1005 | 0.0472 | 0.1097 | 80.2 |
| Coated Steel 3 | 24.176 | 24.1337 | 0.0423 | 0.0985 | 82.2 |
| Coated Steel 4 | 25.7648 | 25.7155 | 0.0493 | 0.1147 | 79.3 |
| Coated Steel 5 | 25.0139 | 24.9684 | 0.0455 | 0.1059 | 80.9 |
| Coated Steel 6 | 26.4503 | 26.4094 | 0.0409 | 0.0951 | 82.8 |

Table 4.
Corrosion properties of Emblica officinalis HCl medium

| Inhibitor Concentration (ppm) | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| 0 | 26.3810 | 26.1101 | 0.2709 | 0.00629 | - |
| 200 | 25.5865 | 25.4980 | 0.0885 | 0.00205 | 67.29 |
| 400 | 25.3893 | 25.3174 | 0.0719 | 0.00167 | 73.43 |
| 600 | 26.0719 | 26.0141 | 0.0578 | 0.00134 | 78.63 |
| 800 | 25.7791 | 25.7320 | 0.0471 | 0.00109 | 82.56 |
| 1000 | 25.4484 | 25.4143 | 0.0341 | 0.00079 | 87.4 |

Table 5.
Corrosion properties of Emblica officinalis in $H_2SO_4$ medium

| Inhibitor Concentration (ppm) | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| 0 | 25.8736 | 25.7175 | 0.1561 | 0.003629 | - |
| 200 | 25.2919 | 25.2417 | 0.0502 | 0.001167 | 67.84 |
| 400 | 25.4551 | 25.4182 | 0.0369 | 0.000857 | 76.36 |
| 600 | 25.4862 | 25.4592 | 0.0270 | 0.000627 | 82.7 |
| 800 | 26.1566 | 26.1351 | 0.0215 | 0.000499 | 86.22 |
| 1000 | 26.3888 | 26.3730 | 0.0158 | 0.000367 | 89.87 |

Table 6.
Corrosion properties of Emblica officinalis in NaCl medium

| Inhibitor Concentration (ppm) | Initial weight W1 (gm) | Final weight W2 (gm) | Weight loss W (gm) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| 0 | 25.4556 | 25.3683 | 0.0873 | 0.002029 | - |
| 200 | 25.8089 | 25.7815 | 0.0274 | 0.000637 | 68.60 |
| 400 | 25.9494 | 25.9308 | 0.0186 | 0.000432 | 78.70 |
| 600 | 25.1391 | 25.1276 | 0.0115 | 0.000267 | 86.84 |
| 800 | 26.185 | 26.1750 | 0.0100 | 0.000232 | 88.54 |
| 1000 | 25.5013 | 25.4973 | 0.0040 | 0.000093 | 95.41 |

## 4. Conclusions

The material selected in this paper mild steel is tested separately for its corrosion inhibition after anodization and after the application of amla extract. Based on the experimental studies it is found that the layer of magnetite ($Fe_3O_4$) formed over the surface of the mild steel sample is adherent and can withstand temperatures as high as 500°C. The SEM analysis of the surface morphology, adhesion test and heat resistance test are proof of this claim. The anodized surface has good corrosion inhibition in different mediums (HCl 67.61, $H_2SO_4$ 78.96, NaCl 82.8). The anodized mild steel is found to be adherent to the surface and it is also found to retain its inhibitive properties up to temperatures of 500°C. The anodized mild steel is also compatible with the organic corrosion inhibitor, the extract of emblica officinalis and provides higher inhibition (HCl 87.4, $H_2SO_4$ 89.87, NaCl 95.41) to the mild steel. Thus it can be concluded that the extract adds additional corrosion inhibition to the anodized mild steel and can be used as an alternative to artificial corrosion inhibitors.

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