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Lawsonia Inermis Performance as Corrosion Inhibitor for Mild Steel in Seawater

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Abstract : Henna (*Lawsonia Inermis*) was investigated as a corrosion protector for mild steel through the immersion in seawater for 60 days. The volume of henna extract incorporated in the coating was varied to 5%, 10%, and 15%. Meanwhile, mild steel grade SS400 are prepared in the dimension of 25 mm x 25 mm x 3 mm and tensile samples with dimension specified by ASTM E8 were polished with 400, 800 and 1200 grit of abrasive paper. Immersion test was conducted in seawater for 60 days at room temperature. The inhibitor used was investigated by performing fourier transform infrared spectroscopy (FTIR) test while corrosion measurements were analyzed by weight loss method and electrochemical impedance spectroscopy (EIS). Tensile test was performed to analyse mechanical loss (tensile stress reduction) of the mild steel before and after immersion. The results revealed that henna has major constituents of lawsone which can retard the corrosion attack on metal surface. The presence of double bond carbon has caused the extract to exhibit a good corrosion resistance behaviour. There were three main functional groups found in henna extract which is phenolic group O-H, carboxylic acid C=O and also aromatic rings C=C. The effect on mechanical strength can only be seen after 30 days of immersion. After 60 days, corrosion protection of henna slows down the corrosion reaction on the metals.
Keywords: Corrosion inhibitor, Electrochemical Impedance Spectroscopy (EIS), Organic coating.

Introduction

Commonly, marine structures such as ships and offshore structures are traditionally made of steel. Steel is an alloy that consists of iron and carbon content between 0.2 wt.% and 2.1 wt.% depending on the grade of steels. However, mild steels were used as steel reinforcement because they have a good strength, hard and can be bent, worked or can be welded into an endless variety of shapes for uses from vehicles (like cars and ships) to building materials. Due to their properties such as cheap, high strength, hardness and easy availability, it is applied in various industries. The applications include nut and bolt, chains, hinges, knives, armour, pipes, magnets and military equipment[1]. However, mild steel has poor corrosion resistance when exposure to corrosive environments. Also, they are susceptible to different types of corrosion mechanism[2,3,4].

Seawater is inherently chemically aggressive. The constructional materials applied in handling and processing seawater system are depending upon the nature of the materials and operational conditions, including desalination plants are subjected to varying degree of corrosion[5]. Besides that, the deterioration of facilities by corrosion is a major problem in construction company, oil and gas industries, ship building and other engineering firms, where mild steel has been widely utilized in most structural shapes such as beams, plates, bars and pipes used in both on-shore and off-shore structure. Considering the severity of the damage caused by corrosion in various engineering fields, there is the need to slowly retard the corrosion process in order to reduce corrosion rate[6].

The use of inhibitor for the purpose of controlling corrosion rate of metals which exposed to aggressive environment is an acceptable practice. The inhibitors used nowadays consist of organic and inorganic materials. The application of the inorganic inhibitor not only gives toxicity effect towards living organism, also it is quite expensive. This toxic effect has led to the use of natural products as anticorrosion agents which are eco-friendly and harmless to environment[7]. In an attempt to search for corrosion inhibitors that are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in acid cleaning processes[8]. Corrosion inhibitors were applied due to their economical and theoretical factors towards corrosion problem[9]. Other than that, plant extracts have been reported have the ability to inhibit metallic corrosion[10].

Instead of using henna as an inhibitor, there is new investigation on the correlation characteristic in mechanical, thermal and optical properties of PMMA-acrylic polyol polymer incorporated with henna extract for coating application. Natural brownish dye colorant was extracted from henna leaves and used as a dye colorant in this paint coating system by using ethanol as a solvent. The findings of this paper shows that the potential time measurement test showed that the dye colorant paint system with 10 wt. % of acrylic polyol have the highest coating resistance against electrolyte penetration. While the colorant paint system with 30 wt.% acrylic polyol performed better in mechanical test such as cross-hatch and impact resistance[11].

A stable organic coating serves as a barrier for isolating steel from moisture, chlorides and oxygen[12]. In order to improve the performance of henna extract as an inhibitor, the use of paint with various concentration of henna is needed as corrosion protection for mild steel from corrosive environment such as seawater. The aim of this research is to study the effect of henna as corrosion protection for mild steel in seawater. Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), weight loss method and tensile test were used in this study.

2. Methodology

Figure 1 shows the flow chart or an overview of the methodology for this study.

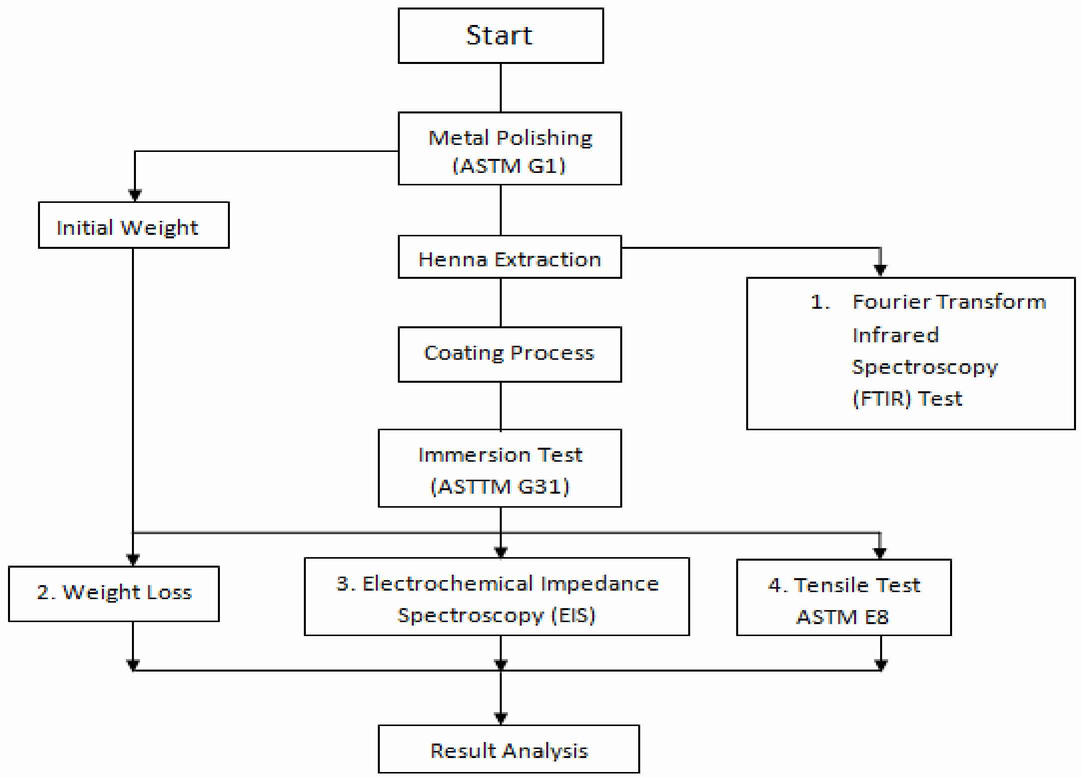


Figure 1: Methodology flow chart

2.1 Specimen preparation

According to ASTM G1 standards, mild steel coupons were cut into square shape with the dimension of 25 mm × 25 mm × 3 mm. The composition of mild steel is 0.22% C, 1.30% Mn, 0.035% S, 0.35% Si, and 0.035% P. Tensile test samples were cut according to ASTM E8 dimension. It was cleaned by using 400, 800, 1200 grit of abrasive paper to remove all loose mill scale, loose rust, loose paint and other loose detrimental foreign matter. Then, the surface of polished sample was cleaned by using acetone and washed with distilled water in order to remove all visible oil, grease, soil, drawing and cutting compounds, and other soluble contaminants. This method is an important step in order to provide good adhesion of the primer to the metallic substrate[13]. Then, the samples were dried in air and the initial weight of the samples was taken. Finally the samples were stored in desiccators.

2.2 Extraction preparation

The commercial henna powders (red henna type) were purchased at a local market. Henna powder then weighed for 100 g each, and ready to be mixed with 300 ml ethanol and left for 7 days with daily agitation. The ethanol extract now filtered through Wattmann filter paper and the remain filtrates were collected and heated in water bath at 48°C to evaporate its liquids content and remove the ethanol from the henna extractions. The residue remains were kept preserved at room temperature until it ready to be used.

2.3 Paint preparation

Firstly, the coating was prepared using binder-based alkyd modified paint. Thinner of 10% was used in this coating system as solvent. The amount of the binder and inhibitor used for this research is shown in Table 1. The incorporated process was done using a magnetic stirrer by stirring the mixture for 24 hours to ensure it is fully blended. This preparation was done in Marine Science laboratories.

Table-1 The formulation of henna coating

Amount \ Coating Type	Bare Metal (control)	5% Henna	10% Henna	15% Henna
Paint (ml)	-	150	150	150
Henna Extract (ml)	-	7.5	15	22.5

2.4 Coating preparation

The coating process was done by using a brush and it was then dried in an oven about 24 hours with the temperature of 70 °C. Then, the thickness control is performed on dry film thickness (DFT) after coating application has been completed. The thickness control checking is performed using PosiTector 6000 thickness gauge. The thickness of the coating is allowed in the range 20 ± 5 µm[14].

2.5 Immersion test

According to ASTM G31 standards, the coated samples underwent immersion test for 60 days at the laboratory using seawater as corrosive media to simulate the real marine environment exposure. Four aquariums were filled with 2.5 litres of seawater in each and kept enclosed to ensure that the seawater was maintained in static condition without external influences. For aquarium 1 it was filled with specimens of bare mild steel, while aquarium 2, 3, and 4 were filled with specimens coated with paint of 5%, 10% and 15% of henna extract, respectively. They were arranged according to the days of specimen's withdrawn. Then, duplicate samples were taken out in every 15 days interval for EIS and tensile test. While for a weight loss method, triplicate coupons were taken out in each 10 days interval. The experiments end after 60 days.

2.6 FTIR test

The FTIR analysis technique was used to provide information about the chemical bonding or molecular structure of materials either in organic or inorganic. 2-3 drops of henna extract were transferred into the sample holder and it was placed in the sample cap of diffuse reflectance accessory. The samples now ready to be analysed by FTIR machines. The extract was exposed under a range of infrared rays beams and the sensor below the platform would sense the frequency either reflected or absorbed. The liquid's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern was then analysed and matched with according to IR absorption table to identify the functional group contained in the henna extract.

2.7 EIS test

Electrochemical Impedance Spectroscopy (EIS) is a technique that characterizes passive films formed on metals or alloys. The passive films formation, dissolution, and breakdown represent one of the most significant features with respect to the corrosion behaviour. EIS was carried out with the open circuit potential, E_{ocp} for every sample. The samples were immersed in seawater (electrolyte) for 30 min over a frequency range of 0.01Hz-100kHz with a signal amplitude perturbation of 5mV and a scan rate of 1 mVs^{-1}. Next, it was fitted with sets of circuits and it is has achieved the stable state of the system with the steady state open circuit potential.

2.8 Tensile test

In this test, a sample was pulled until it reaches the failure state in a relatively short time at a constant rate. The tensile testing was carried out on a hydraulically operated tensile testing machine, having a maximum capacity of 50 kN under static load condition. The load is uni-axially applied to the specimen at a crosshead speed of 10mm/min. The data were collected in a computer control software package. The force data obtain from the chart paper for the tensile test had been converted to engineering stress data, and a plot of engineering stress versus engineering strain was constructed. During the test, the various stress-strain diagrams had been drawn for each of the samples from where the tensile load was determined. The data were used in determining the strength and stiffness of the materials. The tensile test was done for each sample using a universal testing machine according to the standard of ASTM E8. The dimension of the specimen used a dumbbell-like shape followed the range of dimension permitted by ASTM E8 as in Figure 2.

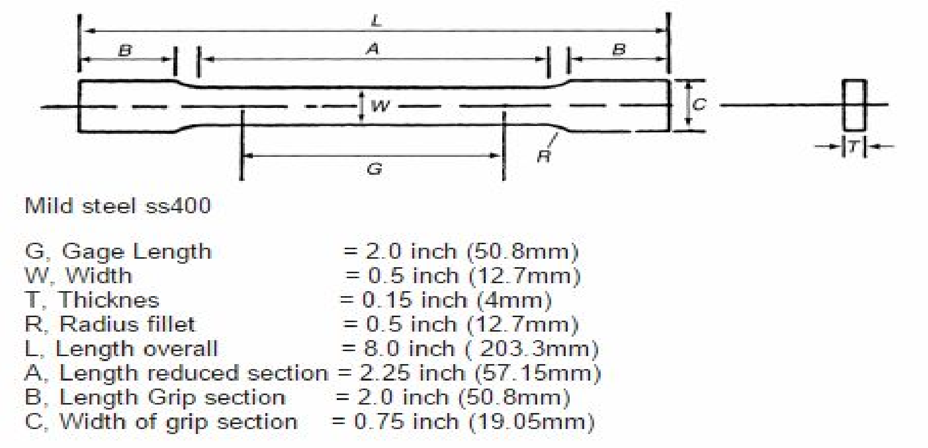


Figure-2 Dimension of tensile sample according to ASTM E8

3. Results and discussion

The data were collected through few methods, including Fourier Transform Infrared Spectroscopy (FTIR), Electrochemical Impedance Spectroscopy (EIS), weight loss method and tensile test. The data obtained were presented in the form of graph and tables.

3.1 FTIR Analysis

According to the IR absorption table, the phenolic -OH stretch appears at frequency 3353.5 cm^{-1}, while the carboxylic acid group, C=O stretching frequency appeared at 1711.9 cm^{-1} and the aromatic rings C=C stretching frequency appeared at 1540.1 cm^{-1}. The other functional group such as alkanes C-H stretching frequency also appeared at 2972.2 cm^{-1}. Thus, lawsone was characterized by IR Spectroscopy (Figure 3). Table 2 summarizes the functional groups found through FTIR process. Meanwhile, double carbon bond in functional group indicates good corrosion resistance in the henna extract. The phenol group of lawsone would donate electron to the metal to achieve its noble state of orbit, while the metal would receive the electron to become more stable. At the same time, this process indirectly retards further redox reaction and could resist metal from corrosion attack[7]. Some researchers have found the organic inhibitors containing multiple bonds in their molecules have the ability of absorb on the metal surface[15].

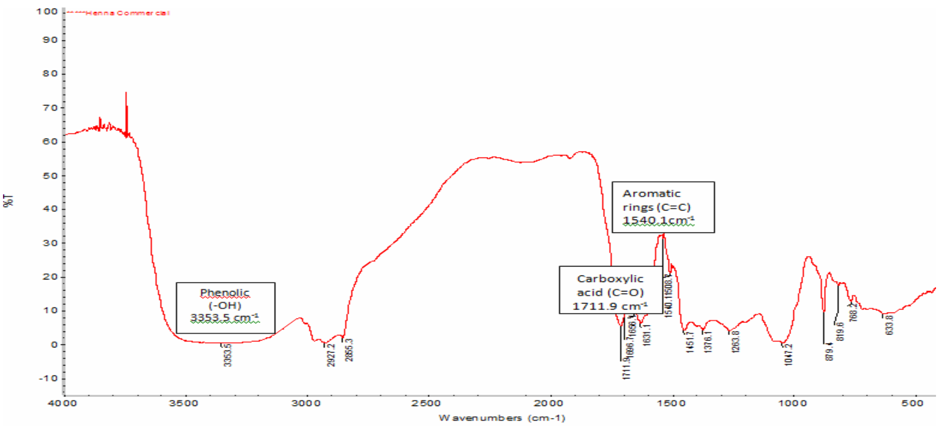
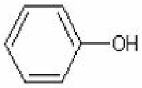
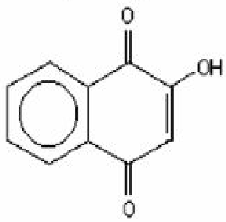
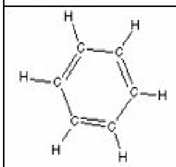


Figure-3 IR spectrum for henna

Table-2 Main components of lawsone identified

Main Functional Group	Major Component
 Phenol O-H	 Structural : Lawsone Molecular Formula : $C_{10}H_6O_3$
 Aromatic Rings C=C	
Carboxylic Acid C=O	

3.2 Weight loss measurement

Based on Figure 4, it was observed that bare mild steel shows a large amount of weight loss during immersion of 60 days, followed by mild steel with inhibitor 5%, 10% and 15%. These indicate that increased in concentration of henna extract in coating system has increased the corrosion resistance which indirectly reduces the weight lost of mild steel. Corrosion rates *(CR)* were calculated by using Equation 1.

$$CR\left(\frac{mm}{y}\right) = 87.6 \times \left(W/DAT\right) \qquad (1)$$

Where:

W = weight loss in milligrams

D = metal density in gcm^{-3}

A = area of sample in cm^2

T = time of exposure of the metal sample in hours

Furthermore, it was found that bare mild steel exposed in seawater has largest weight loss compared with metals with 5%, 10%, and 15% of henna extract. In other words, the greater value of weight loss represented, the higher corrosion occurred. Besides that, Figure 4 shows that the bare metal had encountered the higher redox reaction followed by mild steel protected with 5%, 10%, and 15% of the henna coating in the first 20 days. This could be due to the protection of henna coating at the surface of mild steel, retarding the corrosion initiation process at a metal surface. Higher percentage of henna in coating indicates a better inhibition ability on each metal[16,17,18].

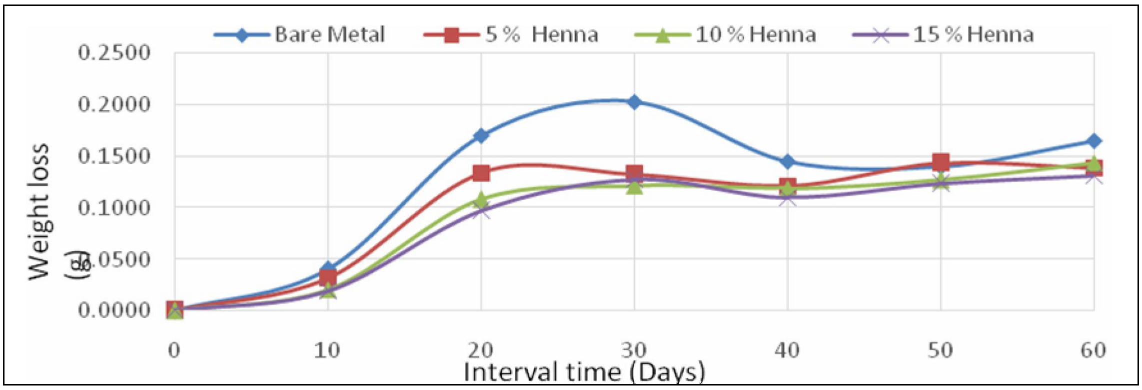


Figure-4 Weight loss of mild steel with different percentage of henna for 60 days

After 30 days of immersion, bare mild steel undergoes slower weight loss and the corrosion rate was maintained until 50 days of immersion. This is due to the reaction of the substrate with oxygen to form metal oxides. This metal oxide was then protecting the surface of mild steel and hence the corrosion rate and weight loss became slower. After 50 days, the weight loss has shown a slightly increase in weight loss until the end of the experiment.

Based on this finding, henna also acted as anodic inhibitor which retards the oxidation to be occurred. Hence, mild steel with higher concentration of henna which is 10% and 15% are able to protect metal surface from corrosion during the immersion period.

The results indicate that the bare mild steel corroded at highest rate compared to the others during 60 days immersion. The presence of 3.5% of chloride ions in seawater contributes to the lower corrosion resistance on metal because of the direct penetration on metal oxide film.

3.3 EIS analysis

The behavior of mild steel coated with 5%, 10% and 15% of henna was studied. The results were analyzed and shown in Nyquist plots. Bare metal acts as a control variable in this experiment. From the EIS test, corrosion resistance of bare metal shows decreases as the time increased.

The Nyquist plots suggest the distribution of capacitance due to inhomogeneities associated with the electrode surface[19]. From Figure 5(a) and (b) it was observed that there are different semi-circle curves formed through frequency response analyzer (FRA). These semi-circle curves show the impedance of the inhibitor by the coating or protection film formed on the mild steel. When the protection film resistance was higher, the semi-circle curve becomes larger. Referring to the Nquist graph, 15% henna shows the largest semi-circle curve as the time increasing until end of 60 days experiment. The increasing inhibitor concentration increases the value of impedance, attributed to charge transfer reaction and also changes the other aspects of the behaviour[20,21]. Thus, the inhibitors do not alter the electrochemical reactions responsible for corrosion but inhibit corrosion primarily through adsorption of inhibitor molecules on the metal surface[22,23]. This results show that the presence of inhibitor improves the protection behaviour of the coating[24]. Other than that, the addition of inhibitor has increased the charge-transfer resistance of coating.

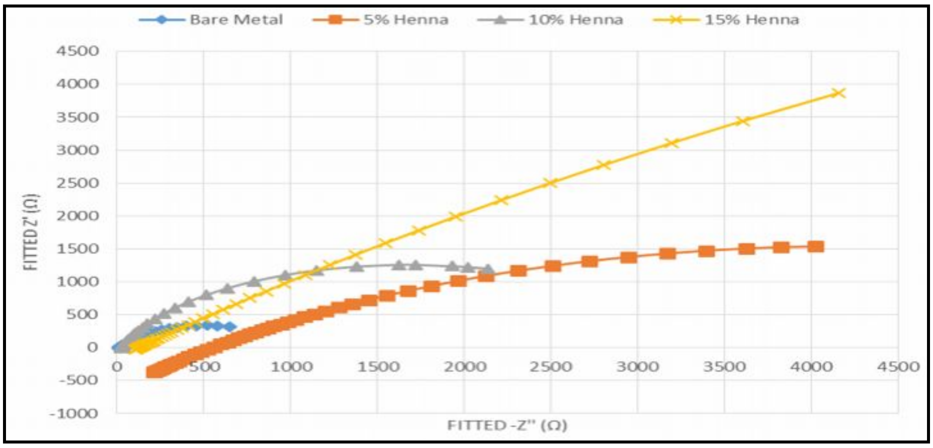


Figure 5-(a) Nyquist plot for 30 days immersion test

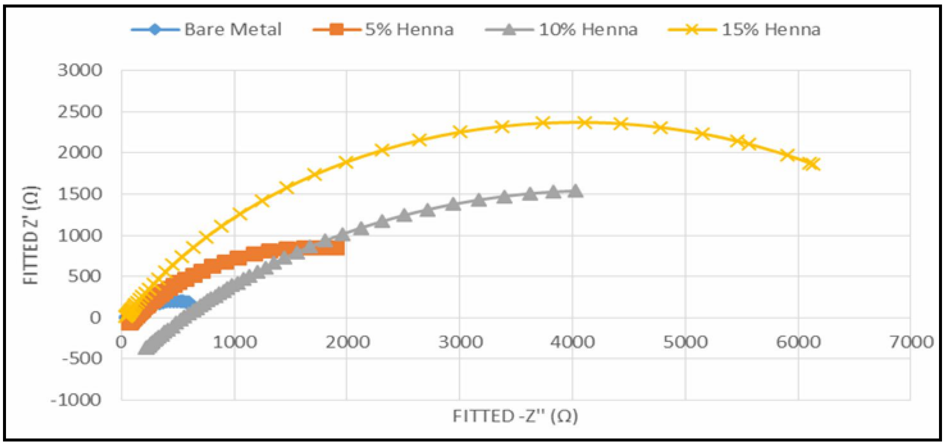


Figure 5-(b) Nyquist plot for 60 days immersion test

The value of charge transfer resistance, R_{ct} (Ω), were obtained from the Nyquist plots. Table 4 shows R_{ct} value of 15% henna lower at day 30th and the value drop when day 60th, indicating the stage of degradation of the coating itself. It was found the table, the value of (R_{ct}) increased with the increasing henna percentage incorporated into paint. This is due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. In addition, the inhibitor acts via adsorption at the metal /solution interface[20,25].

Table -4 Corrosion resistance value of different percentage of henna coating

Immersion days	Day 30th	Day 60th
Resistance / Metal	R_{ct} (Ω)	R_{ct} (Ω)
Bare Mild Steel	809.9	732.8
5% Henna	7427.0	1533.2
10% Henna	3317.7	7427.0
15% Henna	32541	8009.8

3.4 Tensile test

The effects of corrosive media on the mechanical properties of mild steels can be investigated by performing tensile test. A prolonged immersion effect shows a massive difference on the mild steel behavior.

Figure 6 show the graph of ultimate tensile stress (MPa) of different coating against immersion days. Starting from 1 to 15 days, the ultimate stress shows the similar trend for bare and coated metals. This occurs due to the inhibition of henna as a corrosion protection for the metals. After 30 days of immersion, the ultimate tensile stress value slightly decreased since it was exposed to the corrosion. The strength of metals starts to decrease with the presence of corrosion.

The function of henna is to retard the corrosion process and the drastic effect can be seen after 30 days to 60 days of immersion. Table 5 shows the value of the ultimate tensile stress for 60 days. For 5% henna, it deducted from initial value of tensile stress 397.16MPa until 283.3MPa compared to the lowest tensile stress 267.5MPa of bare metal at day 60. While for 10% and 15% henna, the tensile value at day 60 recorded are 297.2MPa and 304.2MPa, respectively. Based on Table 5, tensile stress value decreases as the immersion day increases.

Table-5 The value of ultimate tensile stress against immersion day

Types of Metal	Bare metal	5%	10%	15%
Immersion Period (Day)	Ultimate Tensile Stress (MPa)			
0	397.2	397.2	397.2	397.2
15	349.9	361.8	372.8	374.8
30	316.8	331.9	345.9	349.9
45	288.3	300.1	314.5	319.5
60	267.5	283.3	297.2	304.2

4. Conclusion

As a conclusion, the main components found in henna are phenols O-H at 3353.5 cm^{-1}, carboxylic acid C=O at 1171.9 cm^{-1} andaromatic rings C=C at 1540.1 cm^{-1}. Double carbon bond indicate good corrosion resistance of henna extract. Increasing percentage of henna extracts was able to retard the corrosion within 60 days experiment. 15% henna gives highest corrosion resistance to mild steel. The reducing of tensile strength against immersion day due to corrosion and coating with 15% of henna give a small value of reduction for ultimate tensile stress.

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