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Lawsonia Inermis as green inhibitor for corrosion protection of aluminium alloy

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ABSTRACT

Corrosion behaviour of aluminium alloy inhibited by henna was investigated by using weight loss analysis, Fourier Transform Infrared (FTIR), electrochemical impedance spectroscopy (EIS) and potendiodynamic polarization study. Lawsonia inermis or also known as henna was extracted by using ethyl acetate and methanol. The result from these characterization shows that henna extracted in ethyl acetate exhibits better inhibition towards corrosion. The value for charge transfer resistance, (R_{ct}) decreases as a result of increasing in the degree of protection of AA5083. Double layer capacitance, (C_{dl}) decrease indicates that a layer was form indicating the formation of a surface film. This reflects the inhibitor does retard the corrosion rate. Both solvent extract Lawsone component which is the main constituent of Lawsonia Inermis and both also were able to inhibit AA5083 in this experiment.

I. INTRODUCTION

Synthetic inhibitor which is inorganic inhibitor and also followed by some of the organic compound for inhibitor such as nitrogen, sulphur and oxygen showed significant inhibition efficiency but often available as an expensive element and be capable of bringing harm to environment thus toxic to living beings [1]. So, there should be a research on natural inhibitors where it should be used to overcome this problem. It has been well documented that aluminium alloy 5083 is subjected to 'sensitization' and subsequent attack of grain boundaries resulting in corrosion problems when exposed to seawater. These problems are manifested in a variety of ways, sometimes with cracks in the vicinity of welds or pitting corrosion.

Most of the synthetic compounds show good anticorrosive action yet highly toxic. These inhibitors can bring damage to organ system as a result disturbing a biochemical process and enzyme system in the body. The toxicity possibly will manifest either throughout the synthesis of the compound or during its applications. To prevail over this problem, investigations are established to focus on the usage of natural products where cheap and harmless inhibitors can be found. Finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [2].

Inhibitive action of henna extract (Lawsonia inermis) where its main constituents (Lawsone, Gallic acid, a-D-Glucose and tannic acid) on corrosion of mild steel in 1 M HCl solution was investigated through electrochemical techniques and surface analysis (SEM/EDS). From this research polarization measurements indicate that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration [1].

Previous study where the aqueous extract of the leaves of henna (Lawsonia) was tested as corrosion inhibitor of carbon steel, nickel and zinc in acidic, neutral and alkaline [3]. This study includes analysis data from the extraction of the Lawsonia Inermis which was used to inhibit the aluminium plates. The study involves the effect of different solvents to extract the inhibitor which was used for the immersion test where Lawsonia Inermis was extracted by ethyl acetate and methanol.

II. MATERIALS AND METHODS

2.1 Material

The aluminium alloy type 5083 (AA5083) was used for this experiment. Henna was extracted using two different solvents which were ethyl acetate and methanol using rotary evaporator (Rotavap). The oily residue resulted from the evaporation process using rotary evaporator was used to inhibit the AA5083 coupons. This experiment consist a constant

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concentration of inhibitor which was 200ppm in filtered sea water.

2.2 Weight Loss Experiment

AA5083 was cut into 25mm x 25mm x 3mm and polished manually using 600, 800 and 1200 grit of emery papers. The coupons were degreased using acetone and cleaned with plenty of distilled water. These coupons were weighted before any experiment was conducted. The coupons were hung for 60 days inside several aquarium tanks (300mm x 600mm x 300mm) in 20*L* of filtered sea water. The immersion test was conducted in a room temperature. The data was analyzed for each 10 days of immersion.

2.3Fourier Transform Infrared Spectroscopy (FTIR)

Extract of henna was placed and exposed under range of infrared ray beams. The transmittance and reflectance of the infrared rays at different frequencies was translated into an IR absorption plot consisting of reverse peaks. The spectral pattern was analyzed and matched according to IR absorption table to identify the functional group contained in the henna.

2.4 Electrochemical Measurements

For EIS measurements, the test was conducted by using AC signal of impedance measurements by using Autolab PGSTAT302N and run at the corrosion potential. All the potentials referred were relative to SCE. The impedance measurements were conducted over a frequency range of 1 MHz down to 10 mHz. The results were analyzed using the fit program FRA.

2.5 Potentiodynamic Polarization

Potentiodynamic polarization is the most common polarization method used for measuring corrosion resistant [3]. The cell used was a conventional three electrodes with a platinum wire counter electrode (CE) and a saturated calomel electrode (SCE) as reference to which all potentials were referred. The working electrode (WE) is in the form of a square cut so that the flat surface would be the only surface in the electrode. The potentiodynamic current-potential curves record the data after the electrode potential was automatically changed from -200mV to +200mV with the scanning rate of $10mVs^{-1}$. The results were analyzed using the GPES fit program. Corrosion current (I_{corr}) was calculated by using the Stern-Geary where b_a is anodic Tafel slope [4], b_c is cathodic Tafel slope and R_p is polarization resistance:

$$I_{corr} = \frac{b_c \times b_a}{2.303 R_p (b_c + b_a)} \tag{1}$$

III. RESULTS AND DISCUSSION

3.1 Fourier Transform InfraRed Spectroscopy (FTIR)

Figure 1(a) and 1(b) shows the FTIR for henna extraction by ethyl acetate and methanol solvent, respectively. Henna extracts containing heterocylic which conjugated double bonds. On the other word, this gives the henna extract to be good corrosion resistant for aluminium alloy due to the presence of the double bond carbon. For instance, the main components can be found in the both henna extract by two solvents hydrogen bonded which is phenols O-H, C=O and alkenes C=C. This is the main components which can be found in Lawsone structure.

There are two α,β-unsaturated carbonyl bands at 1735.2 and $1625.1cm^{-1}$ (C=O chelated with an α-hydroxyl) signify the presence of two carbonyl groups conjugated with a double bond (α,β – unsaturated carbonyls) and thus endorsing the possibility of having a 1,4-naphthoquinone [5-6]. It was found that henna consists of a major component which is Lawsone as shown in Figure 2. 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. This indirectly retard further redox reaction and could resist metal from corrosion attack [2].

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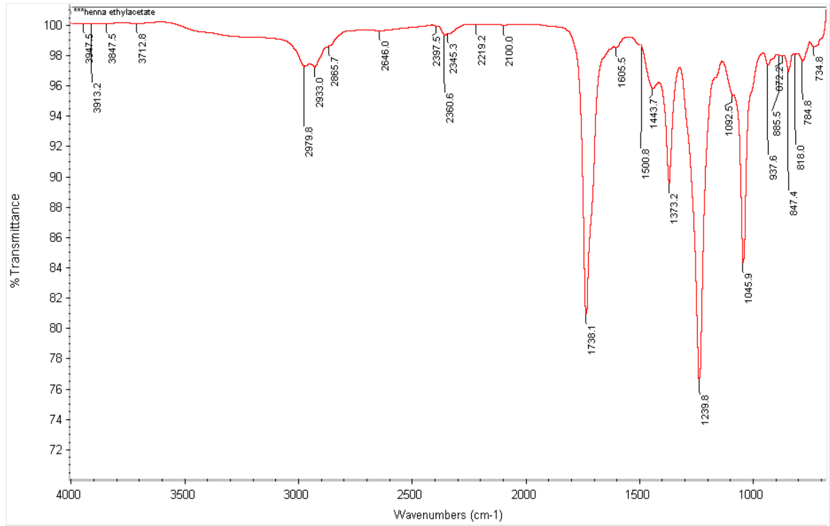
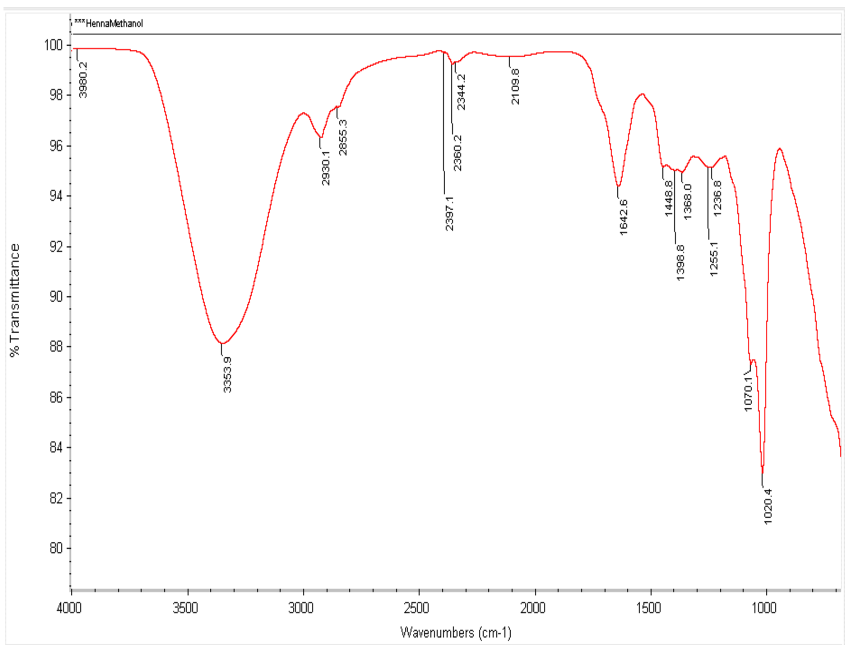


(a)



(b)

Figure 1(a) and 1(b) : FTIR for henna extraction by ethyl acetate and methanol solvent respectively

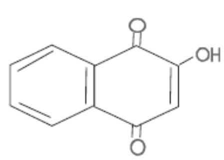


Figure 2: Structure of lawsone

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3.2 Weight loss Analysis

Data obtained from weight loss calculation was analyzed using graphical method. The percentages of weight loss for both parameters have been determined as a function of the immersion time. From Figure 3, control coupons have greater rate of weight loss compared to the addition of henna as the inhibitors. There was a rapid of weight loss for control during 10 days to 20 days. Here can be assumed that the coupons were reacted with the filtered sea water to form a layer which is aluminium oxide (Al_2O_3). This phenomenon is what makes aluminium alloys type 5083 so special. It can instantly create a layer, (Al_2O_3) for corrosion resistance.

The oxide film formed on the aluminium alloy surface is non-uniform, thin and non-coherent. Therefore, it imparts a certain level of protection under normal conditions. When exposed to environments containing halide ions, of which the chloride (Cl^-) is the most frequently encountered in service, the oxide film breaks down at specific points leading to the formation of pits on the aluminium surface [7]. The Al_2O_3 layer managed to protect the control coupons from being attack or react with the filtered sea water only between 20 days and 30 days of immersion time. Between this period, there was a slight change of rate for percentage weight loss. This indicates that a slow activity of corrosion rate has been occurred. After 30 days for control, the corrosion rate increase immediately and continue to increase until 60 days.

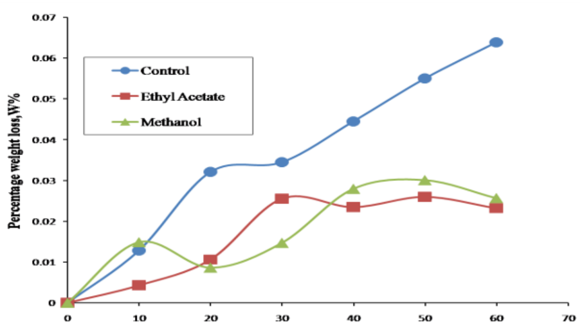

Fig.3. Weight loss percentage versus immersion time

3.3 Electrochemical Impedance Spectroscopy (EIS)

As seen from Figure 4, the plot of impedance shows single capacitive semicircle which indicates the process was controlled by charge transfer [8] and could be assigned to the oxide layer of AA5083.

The data of impedance gained from EIS was tabulated in Table 1. EIS study compares the value of charge transfer resistance, R_{ct} and double layer capacitance, C_{dl}. Higher value of R_{ct} could be attributed to higher efficiency of inhibition where in this case, extract of henna in ethyl acetate shows higher value of R_{ct} compare to extract of henna in methanol.

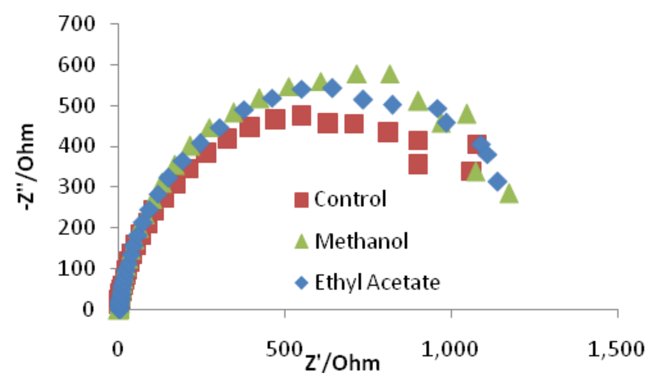

Figure 4: Nyquist plot for AA5083 inhibited by henna

Table 1: Impedance parameter of AA5083

Parameter	R_{ct} (kΩ cm^{-2})	C_{dl} (μFcm^{-2})
Control	1.2828	405.9
Ethyl Acetate	1.2981	342.34
Methanol	1.2916	363.64

The capacitive loop in Figure 4 is due to the charge transfer reaction and time constant of the electric double layer as well as surface inhomogeneity of structural or interfacial origin. This behavior commonly found in adsorption process [9-10]. The decrease in double layer capacitance, C_{dl} is due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer [9]. This process shows that the addition of henna as inhibitor acts by an adsorption at the aluminium and solution [11]. The changes in C_{dl} values can be a sign that there is gradual replacement of water molecules by the adsorption of the organic molecules on the metal surface. Thus, it decreases the extent of metal dissolution [12].

www.ijmer.com Vol.1, Issue.2, pp-723-728 ISSN: 2249-6645

3.4 Potentiodynamic polarization

The effects of henna in different solvent on the corrosion reactions were determined by polarization measurements. The changes observed in the polarization curves after the addition of inhibitor were usually used as the criteria to classify inhibitor as cathodic, anodic, or mixed [13].

Figure 5 represents the I_{corr} value for henna while the data of potentiodynamic polarization was tabulated in Table 2 represent the anodic and cathodic polarization cuves of AA5083 in seawater in the absence and presence of henna.

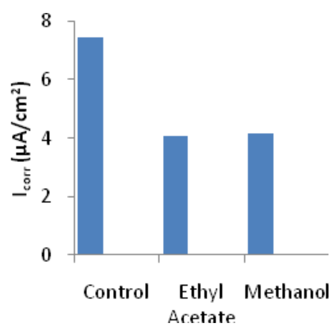

Figure 5: I_{corr} data for henna extracted by different solvent

From Table 2, the corrosion potential, E_{corr} shifted toward more positive direction and toward lower current densities which indicates that henna is a mixed-type inhibitor with predominantly control of anodic reaction [8].

The process of shifting towards more positive value indicates that the inhibitor influence the dissolution of aluminium and the hydrogen evolution process as the inhibitor behaves as mixed-type inhibitor [8]. The change of E_{corr} is assumed to be related to the growth of a passive layer at the surface electrode [14]. The value of cathodic Tafel slopes decrease upon addition of inhibitor which indicates that there are variation of inhibition mechanism occurs in the corrosion process.

4. CONCLUSION

From the results, it can be concluded that henna extract shows mixed type inhibitor but predominantly to cathodic branch. The result shows that henna extract work as good inhibitor for aluminium alloy type 5083. The main constituent in henna that is responsible inhibition effect is found to be Lawsone.

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Table 2: Potentiodynamic polarization gained from Autolab software

Parameter	i_{corr} (µA/cm²)	*bc* (mV/dec)	*ba* (mV/dec)	R_p (Ohm)	E_{corr} (obs/mV)	*Corrosion rate* (mm/year)
Control	7.4335	92.599	126.58	416.6	-877.32	11.118
Ethyl Acetate	4.0447	72.246	90.854	576.2	-876.08	6.0596
Methanol	4.1611	120.68	41.498	429.7	-819.07	6.2552

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