GREEN CORROSION INHIBITOR (THYME OIL) LOADED HNT FOR CORROSION PROTECTION OF CARBON STEEL

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Mechanical Engineering
With Honours

January 2020

Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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January 2020

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Carbon steel is mainly used in any industry applications and always been related to the main problem which is corrosion. New advanced technology is being applied to inhabit the corrosion problem by using the green corrosion inhibitor which using the inhibitor from the natural sources that free from the heavy metal, eco-friendly and mainly will not hazardous and yield any harm to the environment. Nowadays, many studies have been performed regarding to the green corrosion inhibitor where using the natural sources to organic compound such as aromatic herbs, species and medicinal plants. For this paper, experimental works necessary to better understanding on the application of the thyme oil as the main component as green corrosion inhibitor. In this study, the control method will be use is the green inhibitor which by using the thyme oil and also the halloysite nanotubes (HNT) as nanocontainer or host for entrapment of corrosion inhibitors. The green corrosion inhibitor will be loaded into the halloysite nanotubes (HNT) as the major constituents to produce the coating and will be tested on the carbon steel. Hence, this study target to prepare the coating by varying concentration of corrosion inhibitor, time of mixing, HNT concentration in epoxy, to determine and optimize green corrosion inhibitor-loaded HNT concentration which needed to prevent carbon steel from corrosion and investigate corrosion protection and effectiveness of green corrosion inhibitor-loaded HNT as a smart coating. The structural features of the hybrid films were studied by Fourier transform infrared (FTIR). This tests purposely to evaluate the characteristic of the coating and green inhibitor-loaded HNT. In the corrosion testing, will be run by using the Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) measurements to know the efficiency and effectiveness of the coating to prevent from corrosion.

ACKNOWLEDGEMENTS

Praises and thanks to Allah SWT, the almighty, creator, and sustainer of the universe. I would like to thank my supervisor, Dr. Saeid Kakooei for his support, help, and guidance during my study in Universiti Teknologi PETRONAS (UTP). I gratefully acknowledge Suresh Kumar Subhalakshmi for their suggestion, and assistance during my research work and construction of my thesis. I also thank to Universiti Teknologi PETRONAS for the financial support during my whole research.

I also would like to deeply thank to Centre for Corrosion (CCR) staff especially for Mr. Jamalulhaq, for their help in executing my experiments.

Finally, this work could not be completed without the continue support and pray from my whole family especially my father, Mohd Khalid Bin Md Burham and my mother, Nor Salisma Binti Mhd Hairi for their never ending prayer and patience to give me advice, suggestion, and support. Lastly, thank you to my friends who support me through all these past 5 years in university. I am so thankful for our friendship and thank you for being the shoulder I can always depend on.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Corrosion is the degradation of steel by chemical attack and interaction with the environment. It is a persistent and ongoing problem, always difficult to completely eliminate. For example, carbon steel pipelines are used to transport oil and gas to a considerable distance which are then exposed to various corrosive environment, both internally and externally. Internal corrosion in the pipeline can be caused by CO2, H2S, microbiological activity, water chemistry, flow velocity, oil or water wetting and composition, and surface condition of the steel. Prevention would be more realistic and achievable than complete elimination. Prevention would be more practical and workable than complete elimination. Corrosion mechanisms develop quickly after the breakdown of the protective barrier and are followed by a variety of reactions that alter the structure and properties of both the metal surface and the local environment. This has significant consequences in multiple areas, especially in carbon steel application like piping and more. Therefore, the practice of corrosion inhibitor quite popular for coating the surface of desire metal to protect from the corrosion. The smart coating was the chemical compound from the HNT that added with the inhibitor to enhance the property of corrosion inhibitor to prevent from the corrosion [1]. However, some of the chemical use as inhibitor are heavy metal, harm to the environment and hazardous.

In this research, application of green corrosion inhibitor to replace the conventional corrosion inhibitor and loaded it into the HNT to form smart coating. Corrosion inhibitors are protective means against corrosion of metals [2]. A easy way to look at Green Corrosion Inhibitors may be to reflect on the creation, use and disposal of these substances. It looks at the entire life cycle of inhibitors to generate more effectively effective inhibitors with less waste and, mostly, no waste [3]. Most of the corrosion inhibitors on the market that have been used in many businesses are usually generated through chemical synthesis and therefore have a negative impact on the environment. This has prompted many scientists around the world to use new, non-polluting natural molecules in the atmosphere. Therefore, author propose to practise the application of thyme oil as the green corrosion inhibitor in the smart coating application.

Numerous experiments were also performed to research the inhibitory effects of different natural materials against metal corrosion in the steel industries in general : thyme oil [4] . This has driven various scientists worldwide to use sustainable non-polluting through green materials. A few ponder classes were formed to take into account the inhibitory effect of various ordinary substances, in general in metal applications, on the degradation of materials in the industry. The empowering comes about obtained by characteristic compounds as inhibitors of steel corrosion in acidic arrangements driven author to consider various common sources to overcome the corrosion of carbon steel problem. The objective of this paper study is to load the thyme oil as the green corrosion inhibitor into the HNT and test the inhibitory effect of essential oil of thyme on the corrosion of carbon steel in acidic solution.

1.2 Problem Statement

Corrosion inhibitor are widely used in many industries to prevent from the corrosion problems. However, the highly contain metal or hazardous chemical used can affect the environment especially during the discharge process. Due to the environmental concern especially in the application of corrosion inhibitor which mostly contain heavy metal contains, by practising the application of green corrosion inhibitor which proposed by using the thyme oil loaded into the HNT to produce smart coating. By optimizing the loading of green corrosion inhibitor into the HNT and choosing the best concentration of green inhibitor will produce high quality coating. Therefore, this green corrosion inhibitor must have proving the loading processes of the green corrosion inhibitor-loaded HNT and its effectiveness as corrosion inhibitor toward carbon steel application in the acidic solution condition by running some experiments and testing. From the result will show how the efficiency of loading process of green corrosion inhibitor into HNT within vary in concentration of green inhibitor and the effectiveness of green inhibitor-loaded

HNT/epoxy as smart coating can protect the carbon steel from the corrosion reaction. Thus, enhancing the application of the green corrosion inhibitor by replacing the conventional corrosion inhibitor that bring harm to the environment is the promising method.

1.3 Objectives and Scope Study

1.3.1 Objectives

Corrosion inhibitors are a significant and most commonly used and cost-effective method of preventing corrosions, but are always subject to regulation because of its scientific, economical and esthetical significance. Therefore, here author want to give main 3 objective about this study:

1. To investigate green corrosion inhibitor (thyme oil) efficiency in corrosion protection of carbon steel.

2. To evaluate and optimize the loading of the green corrosion inhibitor halloysite nanotube by the variable of concentration of green corrosion inhibitor and time of mixing.

3. To evaluate and analyse the effectiveness of the proposed green corrosion inhibitor-loaded HNT toward the carbon steel protection in corrosive condition.

In this study, author will run a few experiments and testing during the making of the green corrosion inhibitor as the smart coating. The first, loading process of the green corrosion inhibitor which thyme oil into the HNT. In this scope, the component of green corrosion inhibitor will load into the inner lumen of HNT and choose the best concentration for green corrosion inhibitor loaded HNT for producing the high quality smart coating. Second, to test the effectiveness of green inhibitor loaded HNT by the measured parameters and adequate corrosion control performance of the carbon steel in acidic condition and see how this green corrosion inhibitor can reduce the corrosion rate.

1.3.2 Scope Study

The scope of study for this project as per stated below:

1. This project focuses on loading thyme oil into halloysite nanotube and test the effectiveness of the green corrosion inhibitor to protect the carbon steel in coating application and direct injection into test solution.
2. To formulate green inhibitor-loaded HNT as a smart coating, the condition and environment are as stated below:
   - Nanocontainer: halloysite nanotube
   - Green Inhibitor to be loaded: thyme oil
   - Green Inhibitor to be injected: thyme oil
   - Corrosion environment: acidic solution
   - Substrate / material: carbon steel
3. Loading process of the thyme oil into inner lumen of halloysite nanotubes within certain time (hours).
4. Then the green corrosion inhibitor product will be tested the effectiveness to protect the carbon steel in the acidic condition by coating the sample and direct injection of green corrosion inhibitor into test solution.
5. This project is planned to be done in form of experiment. Linear Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR).
6. After the electrochemical test, the surface analysis would be conducted for the sample by using microscopic view to see the corrosion.
7. All the experiment will be conducted at Center for Corrosion Research (CCR), Block I
8. The experiment is expected to be completed within 5 months.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion on Carbon Steel

The A106 is a steel widely used for pipeline transportation systems in the oil and gas industry. However, like any other steel, A106 is prone to corrosion when exposed to corrosive media. A material under corrosion attack will suffer in terms of mechanical properties where the yield strength, tensile strength, and ductility of steel will decrease. A structure weakened by corrosion will carry high risk of failure which will result in accidents .The corrosion phenomenon is damaging to the oil and gas industry where the majority of oil and gas installations are prone to corrosion[5]. Corrosion phenomenon can cause severe pollution to the environment as corrosion at pipelines or pressure vessels can cause leakage or discharge of harmful substances to the environment[6]. Here the corrosion mechanisms of the carbon steel in the acidic solution[7] :

Anodic reactions:

$3Fe+4H_2O \rightarrow Fe_3O4+8H^++8e$

$Fe \rightarrow Fe^{2+}+2e^-$(dissolution of iron)

$Fe^{2+}+H2O \rightarrow Fe(OH)^++H^+$

$3Fe(OH)^++H2O \rightarrow Fe3O4+5H^++2e$

In the presence of Cl−, the hydrolysis of Fe2+ is accelerated, as shown in the reactions below;

$Fe^{2+}+Cl^{2-} \rightarrow FeCl_2$

$FeCl_2+H_2O \rightarrow Fe(OH)++H^++2Cl^-$

$Fe^{2+}+H_2O \rightarrow Fe(OH)^++H^+$

The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:

$½O_2+H_2O+2e^- \leftrightarrow 2(OH^-)$

$H^++e \rightarrow H$

$2H^++2e \rightarrow H_2$

2.2 Green Inhibitor

Nowadays of natural awareness and commercial use of the term ' green, ' it is shocking that there is no consensus on the definition of the term. A simple way of looking at Green Corrosion Inhibitors can be to focus on the generation, use and transfer of these materials [2]. This identifies the entire life cycle of inhibitors in order to produce valuable inhibitors more effectively, where less waste is produced or no waste preferably. One of the most interesting ways to achieve this is often through the use of environmentally benign chemicals or inhibitors that can be part of natural materials after their usefulness. Chemical classes and functional clusters known to be harmful-as well as those that can be bioactivated into harmful substances-should be tampered with in the design of inhibitors. Hazardous contemplations of quality have been used to characterize [8]. These range from non - toxic to moo-harmful. The goal organism will become an issue. The transition to non-metal bearing inhibitors or low-nuclear blockers is found during this symposium without toxic phosphates, chromates and any other heavy metal bearing inhibitors. One of these papers actually negotiates a more favourable component to substitute dangerous carrier.

2.2.1 Characteristic of Green Inhibitor

The utilize of "Green Inhibitors", particularly corrosion and scale inhibitors in industry has been intermittent and developmental. The drift appears to be more reactionary to the show and potential natural controls or maybe than proactive. An endeavour is made to solidify the utilization of "Green" and further talk about the display state of innovation application of "Green Inhibitors"[8] which are (1) Prevention- "It is better to prevent waste than to treat or clean up waste after it has been created." (2) Multifunctional- "Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product." (3) Less Hazardous Chemistry- "Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment."

(4) Design low toxicity products- "Chemical products should be designed to preserve the efficiency of function while minimizing toxicity." (5) Benign solvents- "The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used." (6) Design for Energy Efficiency- "Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure." (7) Use of Renewable Feed Stocks- "A raw material or feed stock should be renewable rather than depleting wherever technically or economically practicable." (8) Reduce derivatives- "Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical / chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste." (9) Catalysis- "Catalytic reagents (as selective as possible) are superior to stoichiometric reagents." (10) Design for Degradation- "Chemical products.

It can be seen clearly the categorize and classified the type of green chemistry and the characteristic of them for easier to choose the main component for the green corrosion inhibitor in this study. Green designing changes existing designing disciplines and hones to those that advance maintainability. Green building consolidates the improvement and implementation of innovatively and financially reasonable items, forms and systems to advance human welfare whereas ensuring human wellbeing and lifting the protection of biosphere as a measure in designing solutions. Thus, the thyme oil already has most of the characteristic from the classified type of green chemistry.

2.2.2 Classification of Inhibitor

In green corrosion inhibitor were classified into two class, organic and inorganic. Inorganic inhibitors ordinarily function without oxygen by passivation. These incorporate chromate and nitrate particles, which can be reduced whereas they oxidize the metal surfaces to make a detached oxide film [9]. Other inorganic compounds require oxygen to work. These incorporate phosphates, silicates, borates, tungstate and molybdates. Killing the use of more naturally toxic compounds just like the chromates and dichromate, and supplanting them with more environmentally neighbourly chemicals, has been the major directional change. Tinplate has scattered degradation owing to flaws and imperfections in chloride solutions. Cerium salts in the hostile medium reduce the susceptibility to pitting of tinplate on cathodic sites by cerium precipitation.

There has been impressive audit of organic erosion inhibitors in a few papers and articles and so will not be gone into detail here. For a few a long time, the investigate on green inhibitors has concentrated on move from the harmful inorganic inhibitors to natural inhibitors. All natural inhibitors per se are not green. Present patterns in inquire about on green natural erosion inhibitors are concentrating on natural materials as erosion inhibitors additionally defined blended items as corrosion inhibitors. An example of this phenomenon is the use of more aliphatic amines and the decrease in the use of aromatic amines. Rather than being used as the free amine, the aliphatic amines are being reacted with long chain acids to form salts, for example with tall oil fatty acid. Chandler describes several nontoxic, non-polluting compounds that can be safely used in environmentally sensitive areas as vapor phase inhibitors [8]. From this literature author can manage to classify the thyme oil as the organic corrosion inhibitor for further study and experiment.

2.3 Loading of Inhibitor into Halloysite Nanotube (HNT)

In the making of the green corrosion inhibitor, the loading process must be run and tested by measured using some experiment to see how the effectiveness of the green inhibitor loaded into the inner lumen of the HNT. Before that, need to explain and familiar the characterize of the HNT and why it was selected to be the entrapment of the green inhibitor and release the inhibitor function during the anti-corrosion application. The halloysite nanotubes are naturally available alumino-silicate hollow cylinders having 15 nm lumen diameter and 0.5-1.0 micron length. Due to its high aspect ratio, the corrosion inhibitors have been packed into hollow halloysite lumen (in acetone medium), which allows for better load and stable releases of the inhibitor. The epoxy-silane coating was used to dope the inhibitor-charged halloysite nanotubes at different levels of charging. The capacity of these nanotubes to release inhibitors of corrosion, when required, inhibited the anodic operation, avoided further disruption and limited the corrosion cycle. In this HNT article also concern and highlight about the green corrosion inhibitor and also the HNT as the best housing for the corrosion inhibitor [10, 11]. Therefore in this paper, the FESEM experiment will be run to see the structure of the final product of green corrosion inhibitor.

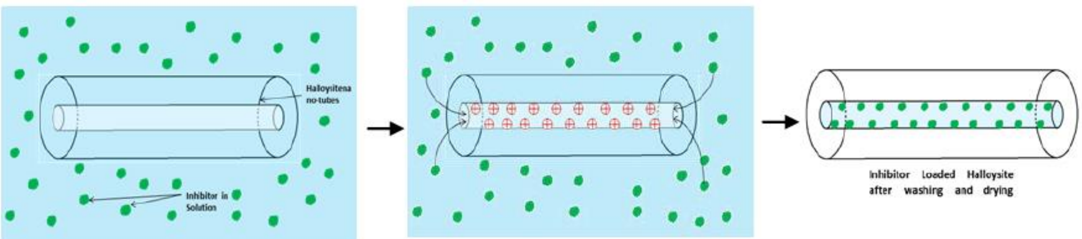


FIGURE 1. The illustration concept of loading inhibitor inside the inner lumen [11].

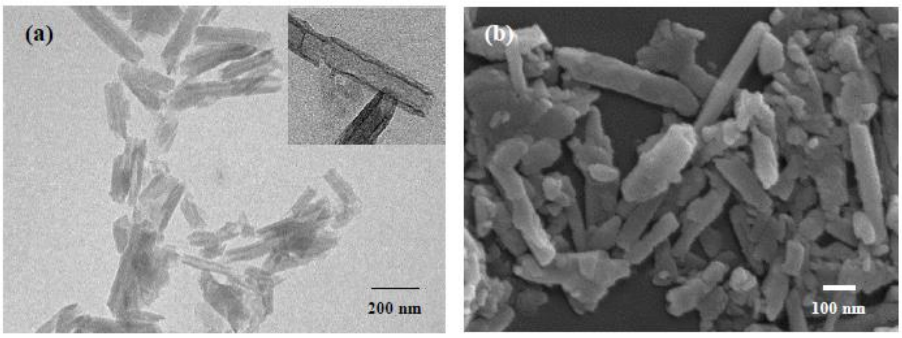


FIGURE 2. (a) Transmission electron mocroscopy image with single HNT enlarge in inset (b) scanning electron microscopy featuring hollow structure of HNT before inhibitor loading [11].

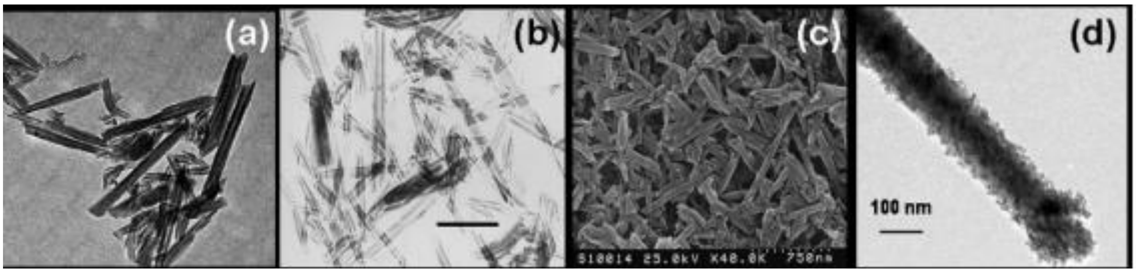


FIGURE 3. (a)(b)(c)(d) The FESEM image of layer-by-layer nanocoating HNT [1]

There the use of halloysite tubes as sedate discharge operators as biomimetic responses vessels as well as additives for organic agents and defensive coats is addressed. Halloysite is used in this context as a nanometer-scalable manager. Halloysite nanotubes can be provided with thousands of tons and are still existing or new natural nanomaterials that can be used for the processing of anticorrosion and biocide specialists of metals and plastics [1]. The pipe reveals broken ends and cracks in locations with structural flaws, and a defensive metal layer is removed from the barrier. The loading method of the nanotube is simple; just an exacerbator and a vacuum pump are needed. Filling efficiency varies depending on the type of molecule to be loaded.

2.3.1 Characteristic of HNT

Halloysites are cost-effective, readily usable, stable, mechanically strong and biocompatible. However, the chemistry of the inner and outer surfaces and liquid potential within nanoscale volumes, which is most important for controlled encapament and release, are not well examined. Metal corrosion, particularly in the aviation, automotive, construction and oil industries, is one of the major destruction processes. Recent advances in surface science open up modern ways for the development with coatings of complex anticorrosion characteristics through incorporation of nanoscale holders (carriers) packed onto established "passive" protective films with inhibitors or other effective compounds, while engineering totally unuseful coating systems based on the "passive" / "active" holder configuration[12]. The primary aim here is to create nanoscale holds that can induce degradation whether externally (e.g., mechanical harm) or internally (e.g. pH changes). 18 In the case that changes are made in the immediate world, or that the oxidation process starts on a metal's surface, the blocker encapsulated should be discharged into the damaged area to carry out self-healing.[13]

TABLE 1. The detailed data of halloysite nanotubes (HNTs)[14]

Molecular Formula	**$Al_2Si_2O_5(OH)_4 \cdot nH_2O$**
Length	100–2000 nm
Inner diameter	10–30 nm
Outer diameter	30–50 nm
Aspect ratio (L/D)	10–50
Young's modulus of a single HNTs	130 ± 24 GPa
Elastic modulus	460 GPa
Interlayer water removal temperature	400 °C
Water contact angle	10 ± 3°
Specific surface area	22.1–81.6 m^2/g
Total pore volume	0.06–0.25 cm^3/g
Density	2.14–2.59 g/cm^3
Mean particle size in aqueous solution	143 nm

In a study of the supramolecular adduct of HNTs and deoxyribonucleic acid (DNA), it is reported that halloysite is stable molecules towards acidic, basic aqueous suspension and also stable at normal temperature and in pure water. In 1M sulfuric acid (H2SO4) solution, the halloysite nanotubes start to dissolve from the inner surfaces of halloysite nanotubes, and as a result amorphous spheroidal nanoparticles of silica (SiO2) are formed, whereas, in 1M sodium hydroxide (NaOH) solution, the halloysite nanotubes start to dissolve from inner surface but results in the formation of aluminium hydroxide (Al(OH)3)[15] . Current study findings suggest that halloysite are nontoxic and chemically are stable for the cells having outer diameter of 50 to 70 nm, inner lumen diameter of 15 nm and length of 1 to 0.5 μm. To improve halloysite nanotubes' interactions, these can be functionalized by different modification methods like covalent functionalization, non-covalent functionalization, etc. The chemical formula of halloysite nanotubes is Al2Si2O5(OH)4.2H2O. HNTs have a nanotubular geometry which exhibit its dimensions on nanoscale. This nanotubular array of HNTs varies with different regions[16].

2.4 Smart Coating

The corrosion inhibitors were loaded into the hollow lumens of halloysite (in acetone medium), which enables higher loading and sustainable release of inhibitor, due to its high aspect ratio. The inhibitor-loaded halloysite nanotubes were doped in the epoxy coating at different loading levels. The ability of these nanotubes to release the corrosion inhibitors as and when required suppressed the anodic activity, thereby preventing the coating from further damage, and restricting the corrosion process[11]. The smart self-healing anticorrosion performance of the epoxy coating loaded with varying amount of halloysite entrap. Until intact, the anticorrosive coatings provide passive protection by acting as physical barrier between the corroding material and the corrosive environment. In contrast, active protection functions provide protection in the presence of an inhibitor by suppressing the corrosion activity even when the main barrier has been damaged. The mechanism of such action varies with the type of inhibitor used, that is anodic, cathodic or adsorption[17]. The two important functions of the halloysite nanotubes was to release the loaded inhibitor intelligently at the site of corrosion due to local pH change, suppressing the corrosion activity and prevent the interaction of inhibitor with the epoxy coating matrix leading to undesirable reaction and deactivation of inhibitor powered was investigated on the mild steel substrate by direct exposure to corrosive media[11]. The EIS and potentiodynamic polarization tests confirms superior barrier property and corrosion resistance offered by coating doped with 1% inhibitor loaded halloysite nanotubes, compared to neat epoxy-silane coating[18]. The improved corrosion resistance can be attributed to the release of inhibitor on demand from the halloysite nanotubes at the site of damage, suppressing the corrosion activity[16].

2.5 Effectiveness of Green Inhibitor Loaded HNT

Some of the advantages of using HNT are as follows: (1) biocompatible, non-toxic, natural. (2) have high surface area, good dispersion capability. (3) able to withstand release if no triggered. (4) able to keep active agent during processing. (5) able to load by several active agent simultaneously. (6) reduce the amount of active agent which is quite costly. (7) can be implemented in various forms such as powders, creams, gels, lotions, and sprays. (8) the high rate of loading, high capacity, and fast adsorption rate. (9) high aspect ratio, no swelling, and contains lots porous (10) increase effectiveness[13].

Thus, in the process of the loading of green corrosion inhibitor which is the thyme oil as the inhibitor into the HNT, a few experiments will be run to measured and analysis the result of the loading efficiency. One of the test will be the TGA where the change of the weight lost in the constant temperature. From certain article prove that the loading of green corrosion inhibitor into the HNT give the positive result. The figure 3 show the one of the result to show the mass lost from the TG analysis experiment.

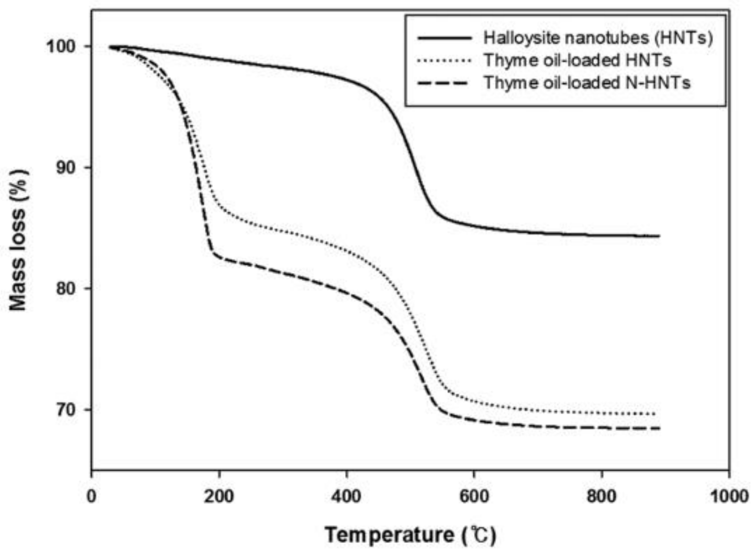


FIGURE 4. TG analysis of the thyme oil loaded HNT capsule [17]

The quantification of the thyme oil was determined using a calibration curve, and the encapsulation efficiency and the loading capacity were obtained from the following equations [17]:

$$\text{Encapsulation efficiency (\%)} = \frac{Mth}{Mo} \times 100$$

EQUATION 1. Encapsulation efficiency

where Mth and M0 are the mass (mg) of thyme oil encapsulated into the HNTs and the initial mass (mg) of the thyme oil added, respectively. This show the efficiency of the thyme oil into the HNT where almost 90% inhibitor is entrapping into the inner lumen of HNT. TGA analysis on HNTs, thyme oil-loaded HNT capsules, and thyme oil-loaded N-HNT capsules. The TGA curve of raw HNTs shows a mass loss in a single step at ca. 500 °C. In addition, the mass loss of incorporated thyme oil was higher in thyme oil-loaded N-HNT capsules than the mass loss of thyme oil in thyme oil-loaded HNT capsules. This result is evident that more thyme oil loaded into the N-HNT than raw HNT and is consistent with the result from GC analysis [17].

Another experiment regarding to the loading process of the thyme oil into the HNT is the FTIR test where infrared light for imaging specimens and analysing chemical properties is used in FTIR research. In one article show that the experiment of FTIR toward the thyme oil [19].

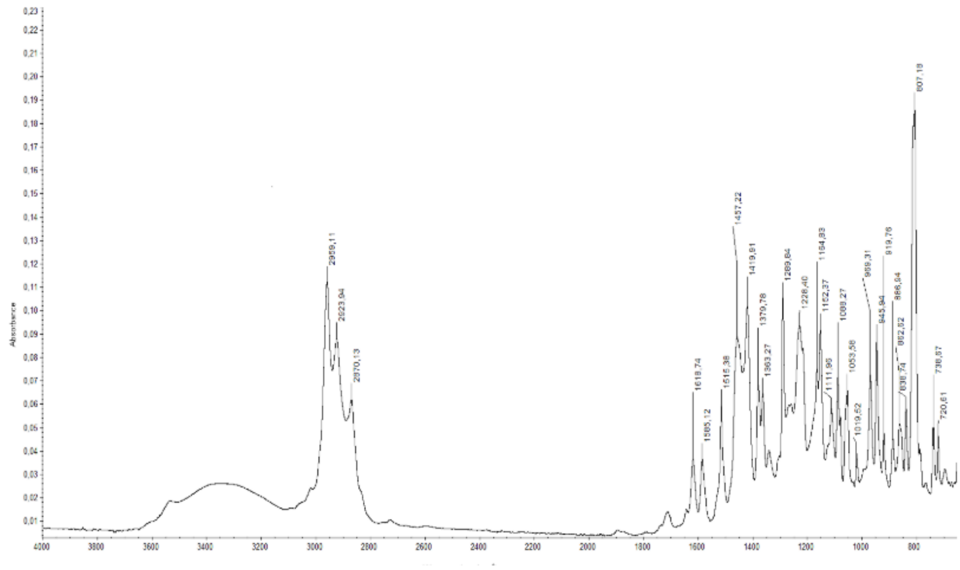


FIGURE 5. FTIR analysis of the thyme oil [19]

The main reason of the selection of the thyme oil as the green corrosion inhibitor it was biodegradable, organic corrosion inhibitors do not include heavy metals or other compounds with toxicity. Several research groups also indicated that naturally occurring substances have been widely used to stop metal oxidation in acidic or alkaline conditions. Research in corrosion is focused on “eco-friendly corrosion inhibitors” that show a low risk of environmental pollution, with good inhibition efficiency. The term ‘‘eco-friendly inhibitor’’ or “green inhibitor” refers to substances that are biocompatible, such as essential oils, since they are of biological origin. Eco-friendly inhibitors can be used in the form of pure compounds. The two major constituents of the studied thyme oil were thymol (29.4%) and p-cymene (21.6%) (Table 2). According to Burt (2004), thyme oil consists of 10 to 64% thymol and 10 to 56% p-cymene. Another two major components reported by Burt are carvacrol (2 to 11%) and γ-terpinene (2 to 31%). The former constituted 4.2% of the essential oil used [19].

TABLE 2. The Thyme oil composition [19]

[%]	RI	RI ref	Component
3.8	933	936	α-Pinene
0.1	946	950	Camphene
0.8	972	978	β-Pinene
0.1	986	987	Myrcene
0.1	997	1002	α-Phellandrene
3.0	1005	1010	3-Carene
0.2	1010	1013	α-Terpinene
21.6	1015	1015	p-Cymene
9.8	1022	1024	1,8-Cineole
6.6	1024	1025	Limonene
0.3	1053	1051	γ-Terpinene
0.7	1086	1086	Linalool
0.2	1129	1126	Cis-limonene oxide
0.5	1143	1142	Isoborneol
2.0	1152	1150	Borneol
2.1	1175	1176	α-Terpineol
0.7	1181	1188	γ-Terpineol
1.6	1243	1239	Linalyl acetate
29.4	1274	1267	Thymol
4.2	1281	1278	Carvacrol
0.2	1406	1411	Longifolene
2.8	1419	1421	β-Caryophyllene
0.2	1452	1455	α-Humulene

RI– Retention indices; RI ref– reference retention indices.

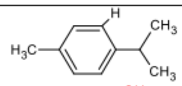
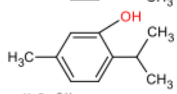
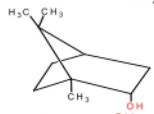
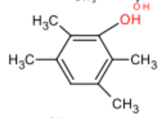
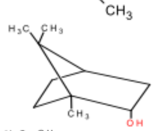
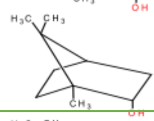
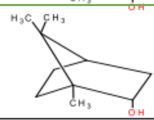
In other study also show the same result of the thyme vulgaris oil composition where the main or major product of the thyme oil was based from one type of composition which are the thymol. From the compound extraction show that the same type of major component in the thyme oil [4].

Most of the experiment were run and tested on the mild steel metal type this is because it was commonly used in many industries. Mild steel is also known as carbon steel, a low carbon steel of superior strength (0.3 percent). It is used when large amount of steel is needed and can be twisted and welded into an infinite range of shapes for uses in vehicles, construction material and vessels fabrication etc. In many sectors, mild steel (MS) is the material of choice in the manufacture of reaction pipes, storage tanks, etc., which are frequently corroded in the presence of acids. The substances of hydrochloric acid are widely used in several industrial processes, including the selection of acid in metal, washing and refining of chemical products, extraction of coal and acidification of oil wells.

Inhibitors are widely used to mitigate the corrosive impact on metallic structures as a consequence of general acid attacks [3].

Metals and alloys are often protected by application of suitable organic or inorganic coatings. This layer can passively or actively inhibit the destructive corrosion surface cycle. Until the anti-corroding coatings remain intact, they offer active resistance through the use of the corrosive atmosphere as a physical barrier. In addition, active protection mechanisms shield the receptor if corrosion behavior is inhibited, even when the key barrier is destroyed. The mechanism of such action varies with the type of inhibitor used, that is anodic, cathodic or adsorption. Industrially, the most effective corrosion inhibition method is the application of chromate based pre-treatment primers or conversion coatings. This figure show how the efficiency for every type of the metal within the essential oil which is the thyme oil. It show the highest inhibitor efficiency is thymus satureioides toward carbon steel.

TABLE 3. Percentage of corrosion inhibition for some essential oils obtained from Thymus derivatives in acidic media on different matrices [20]

Essential oil	Material	Test solution	Optimum concentration	Inhibition efficiency	Geographic location	Major composition	Structure	Reference
Thymus capitatus	Mild steel	1 M HCl	5 mL L^{-1}	65.5%	North-East of Morocco	p- Cymene		[18]
Thyme vulgaris	Mild steel	1 M HCl	2 g L^{-1}	93%	South of Morocco	Thymol		[19]
Thymus algeriensis	Mild steel	1 M HCl	1 g L^{-1}	91%	Eastern of Morocco	Borneol		[20]
Thymus sahraouian	Mild steel	1 M HCl	2 g L^{-1}	76.73%	South of Morocco	Durenol		-
Thymus pallidus	Carbon steel	1 M HCl	1 g L^{-1}	88.75%	South of Morocco	Borneol		[21]
Thymus satureioides	Tinplate	0.5 M HCl	6 g L^{-1}	87%	South of Morocco	Borneol		[22]
Thymus satureioides	Carbon steel	0.5M H_2SO_4	2 g L^{-1}	95.97%	South of Morocco	Borneol		[23]

In addition, the effectiveness of the green corrosion inhibitor must be prove by running a two type of experiment to show the green corrosion inhibitor can protect the carbon steel from the corrosion. Some of the research about applying the thyme oil as the green corrosion inhibitor and tested on the mild steel and show the positive result. Extracting the thyme oil and making the standard composition test to show the component inside the thyme oil. Then, running the experiment to show the properties of the component to be a green corrosion inhibitor. In this paper also show the LPR and also EIS experiment to show the effectiveness of the green corrosion inhibitor. One result was found where showing the different concentration of the thyme oil inhibitor can give different result of the corrosion efficiency where the higher the concentration, the higher the efficiency. The inhibition efficiency IE% of the compounds tested is defined by the following equation [21]:

$$\text{Inhibition Efficiency} = \frac{Rp(inh) - Rp0}{Rp(inh)}$$

EQUATION 2. Inhibition Efficiency

where Icorr and I'corr, respectively, represent corrosion current densities determined by extrapolation of the straight Tafel corrosion potential without and with addition of the inhibitor.

TABLE 4. Corrosion rate and inhibitory efficiencies of thyme oil [21]

	Concentration of inhibitor/ (ppm)	W/ (mg/cm^2h)	EI(%)
Blank	0	0.09375	———
Essential oil of *Thymus Satureoides*	200	0.08159	12.97
	400	0.07445	20.59
	600	0.0609	35.04
	800	0.05499	41.34
	1000	0.03036	67.62
	1200	0.01217	87.02
	1400	0.01217	87.02

This study will be conducted to determine the rates of carbo-steel corrosion of Linear Polarization Resistance (LPR). The related polarization parameters and inhibition performance of carbon steel corrosion. The performance of the inhibition improved while the strength of the oxidation current declined at elevated oil concentrations. This could be understood by adsorption of oil on the surface of mild steel and by the adsorption mechanism strengthened with that concentration of an inhibitor. The raise in E(%) with an increase in temperature as the shift in the structure of adsorption mode decreases, whereas chemical absorption is preferred as the temperature rise [4, 12]. Polarization studies have demonstrated that oil is a mixed inhibitor and increases its inhibition effect with the concentration of the inhibitor. Impedance implies the adsorption of oil on the mild steel substrate with increasing resistance to transition and a decreased capacitance of double sheets. Electrochemical approaches and gravimetric methods are in good agreement about the efficiency of the inhibitor. From the two articles use the same method which is the LPR analysis.

Conclude that the addition of the tested compound causes a slight shift of the corrosion potential but with a tendency towards the cathode values. This displacement is accompanied by a net decrease of the densities of anodic and cathodic current which is more marked when the concentration of the inhibitor increases. On the other article with using the same experiment which is PLR and similar green corrosion inhibitor show the quite similar result [21].

Both articles using the same measured experiment and also same type of green corrosion inhibitor. This show the effectiveness of thyme oil application as the green corrosion inhibitor was promising and give the desired result. Another method to analysis the efficiency of the green corrosion inhibitor is by using the EIS test. In order to evaluate the performance of the compounds tested as a potential deterrent against metal corrosion, the Electrochemical Impedance Spectroscope (EIS) gives information on the interface resistive and capacitive behaviour. It measures 2 phenomena which are the deterioration of organic coating by exposing in an electrolyte and the increase in corrosion rate of the metal surface due to the deterioration of coating and subsequent attack by the electrolyte [22].

A capacitor is developed when two conductive sheets are separated by a non-conductive medium called the dielectric. The capacitance value relies on the plate size, the distance between the plates and the dielectric properties. For a coated metal immersed in an electrolyte, the metal is one plate, electrolyte is second plate, and coating is the dielectric.

$$Capacitance, C = \frac{\mathcal{E}_0 \mathcal{E}_r A}{d}$$

where:

$\mathcal{E}_0 = Electrical\ permitivity$

$\mathcal{E}_r = Relative\ electrical\ permitivity\ (Dielectric)$

$A = Surface\ of\ one\ plate$

$d = Distance\ between\ two\ plates$

EQUATION 3. Capacitance

Plus to calculate the efficiency of the inhibitor by using this following equation :

$$Inhibition\ Efficiency = \frac{CR\ unhibited - CR\ inhibited}{CR\ unhibited}$$

EQUATION 4. Inhibition Efficiency Equation

TABLE 5. Impedance parameters for mild Steel in 1M HCl for various concentrations of T vulgaris oils [4]

Inhibitor	Concentration (g/l)	R_t ($\Omega.Cm^2$)	C_{dl} ($\mu F/cm^2$)	E_w (%)
T.V	1MHCl	21,63	149,8	-
	2	348,89	11,03	93 %
	1	232,28	16,23	89 %
	0,5	201,67	17,03	88,4 %
	0,25	181,34	20,1	87 %

As the levels of receptors increased, rt values decreased. The Cdl values decreased, on the other hand, with the increased concentration of inhibitors resulting in inhibitions efficiencies. This condition resulted in an increase in the inhibitor's surface layer, which resulted in an increase in inhibition output. This reduction in Cdl may result in a decline in local dielectric constant and/or an improvement in the thickness of the double electric layer, which means that the oil works by adsorption on the solution. It conclude that the positive result as the thyme oil as the green corrosion inhibitor that could reduce the rate of corrosion of the carbon steel.

CHAPTER 3

METHODOLOGY

3.1 Flow Chart of Study

This research work consists of laboratory experiment, characterization, and data analysis. The laboratory experiment includes loading inhibitor, coating preparation, corrosion protection measurement, corrosion inhibitor performance, coating performance analysis, and characterization. The workflow is as shown in Figure 6:

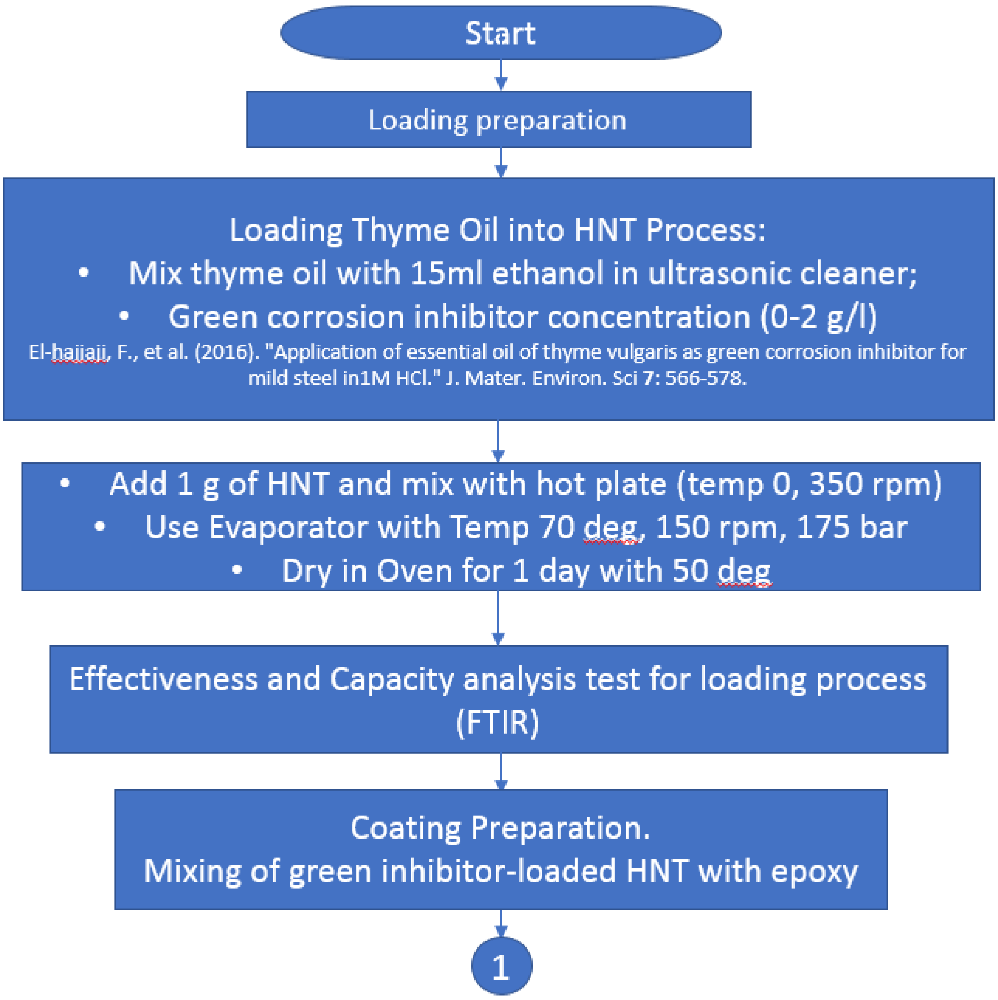
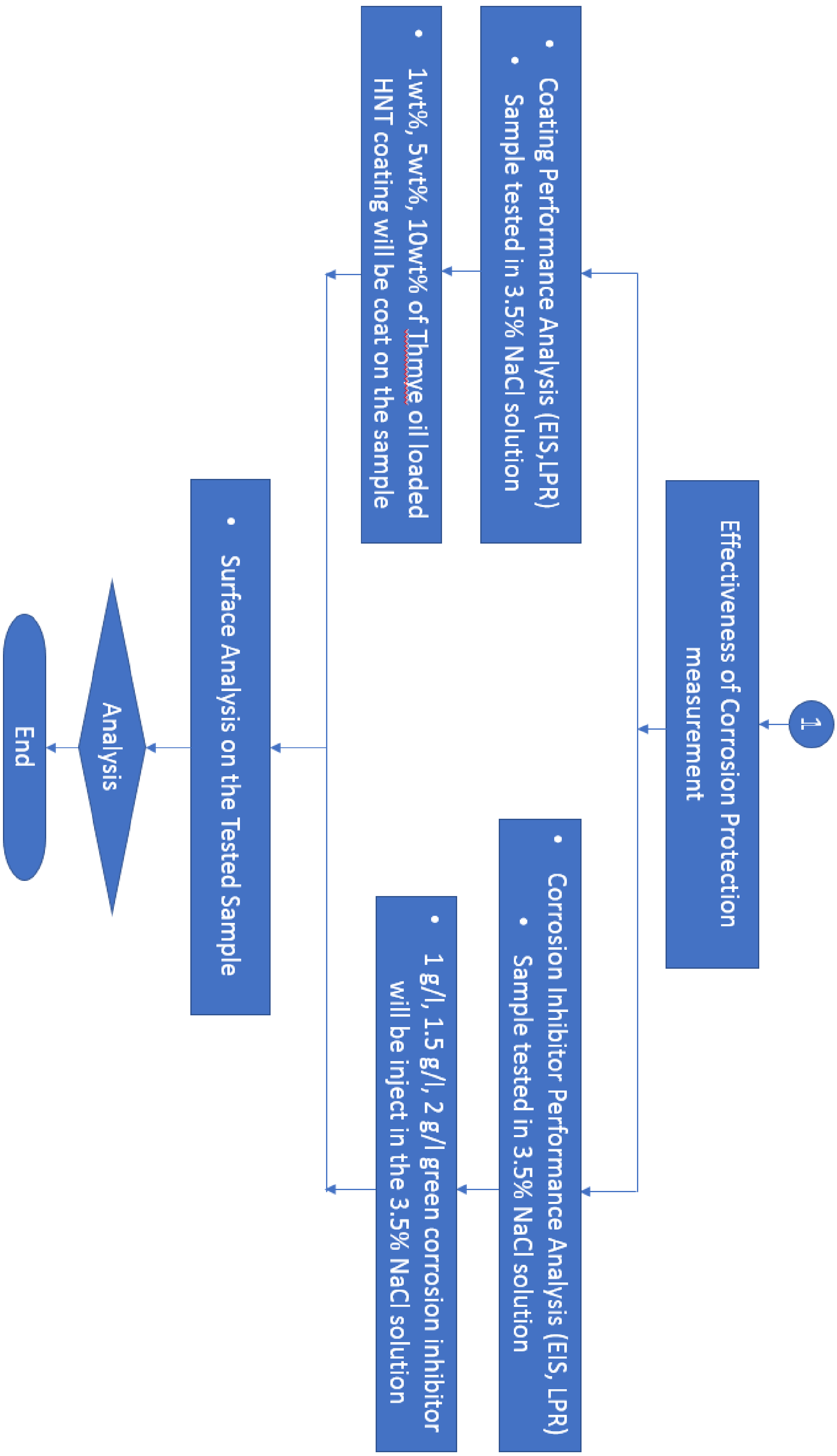


FIGURE 7. Process Flow For Project


1
Effectiveness of Corrosion Protection measurement
Coating Performance Analysis (EIS,LPR)
Sample tested in 3.5% NaCl solution
1wt%, 5wt%, 10wt% of Thmye oil loaded HNT coating will be coat on the sample
Corrosion Inhibitor Performance Analysis (EIS, LPR)
Sample tested in 3.5% NaCl solution
1 g/l, 1.5 g/l, 2 g/l green corrosion inhibitor will be inject in the 3.5% NaCl solution
Surface Analysis on the Tested Sample
Analysis
End

3.2 Sample Preparation

The sample used in this experiment is A106 carbon steel. The sample preparation process is done by preparing 8 specimens of 10 mm (length) x 10mm (width) x 5mm (height) by milling and cutting. Figure 7 shows the samples prepared through machining.

FIGURE 7. Sample with 10 mm (length) x 10mm (width) x 5mm (height)

The samples were then mounted using epoxy resin and each connected to a copper wire as Figure 8 and 9 below.

FIGURE 8. Copper wire connected to the sample by soldering

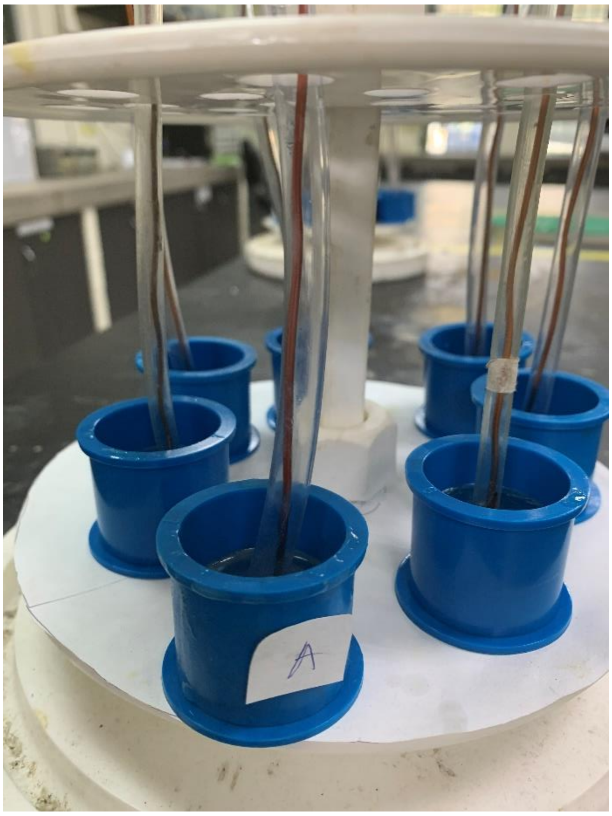


FIGURE 9. Mounted sample with the epoxy

The samples were polished with abrasives grit paper number 80,240,320, 600, 800 until a shiny, flat and smooth surface is achieved and degreased with acetone and rinsed.

Figure 10 below shows the specimens being grinded with abrasives paper.

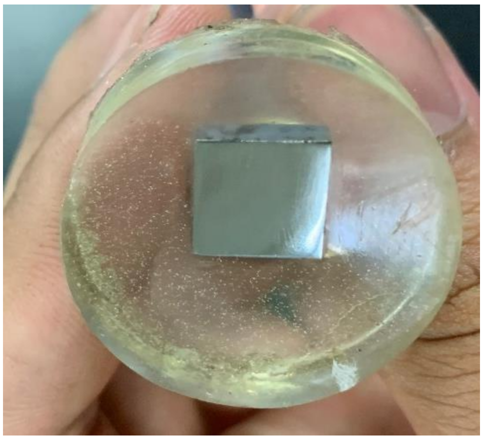


FIGURE 10. Grinded Sample Until Grid 800

3.3 Loading Process of Thyme Oil as Green Corrosion Inhibitor into HNT

Loading of thyme oil green inhibitor into the inner lumen of halloysite nanotubes was performed as per the procedure described elsewhere [11]. Systematic optimization to improve the loading efficiency of inhibitor in the inner lumen was conducted with loading time from 15 minutes at the ultrasonic cleaner, 10 minutes at evaporator and 24 hours in dryer. The thyme oil with different concentration in 15 ml of ethanol solution, then mix by using the ultrasonic cleaner for 15 minutes at 0^{o} temperature as in Figure 11:

FIGURE 11. Mixed thyme oil and ethanol by using ultrasonic cleaner

Then 1 g of dry halloysite nanotube was mixed in the solution and stir by using hot plat and magnetic stirrer for 15 minutes at 350 rpm. The loading of thyme oil into HNT will be conduct by using the evaporator where all the ethanol will be evaporated. The thyme oil loaded HNT will be left in the other flask. The condition for this process were temperature 70^{o} , with rotation 150 rpm, vacuum atmosphere at 175 mbar as per Figure 12.

FIGURE 12. Thyme oil loaded HNT and ethanol in the evaporator

After 5 minutes, shake the flask contained thyme oil loaded HNT and put in the plate then place it in the dryer for 24 hours with 50^{o} temperature as per Figure 13.

FIGURE 13. Dry thyme oil loaded HNT in the dryer

FIGURE 14. (1) 1g/l TO HNT (2) 1.5g/l TO HNT (3) 2 g/l TO HNT which Final product of thyme oil loaded HNT with vary concentration

3.4 Coating Preparation

Different coating condition will be made to compare and determine the effect of smart coating. The samples are divided to samples without coating and good coating. The samples were made by varying the concentration of corrosion inhibitor , mixing time (15 minutes - 24 hours). Then will mix with the in epoxy . Coating material will be made by mechanical mixing of epoxy, hardener, and inhibitor-loaded HNT. Before mixing, epoxy and hardener respectively dissolved in acetone with a ratio of 1:1. Inhibitor-loaded HNT will be incorporated in the acetone solution, then will be stirred at room temperature for certain time. After that, epoxy and hardener will be mixed, then the solution will be added into rotary evaporator to remove acetone. Metal substrate will be dipped into that mixture and dried at room temperature. The process of making the coating material refers to studies conducted.

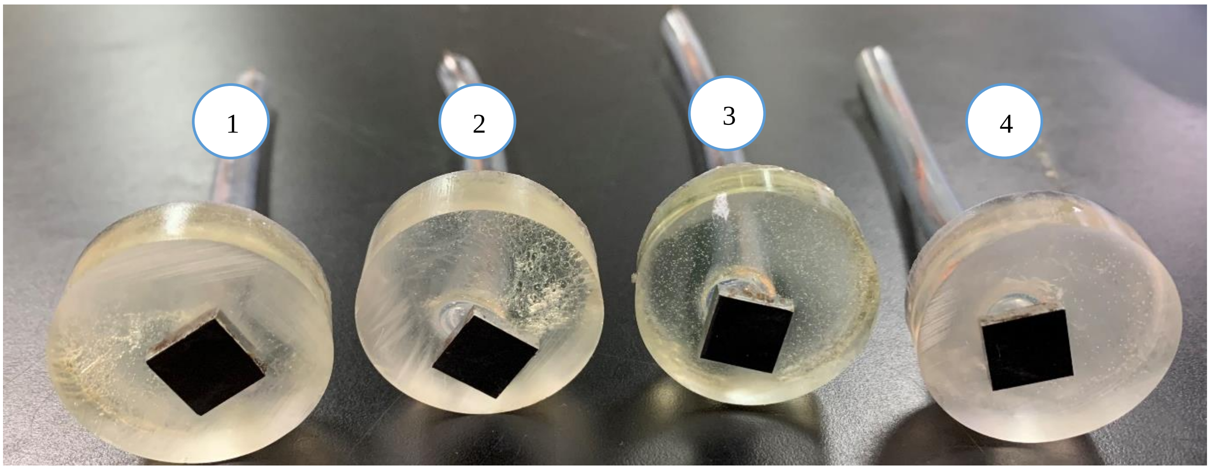


FIGURE 15. (1) 0 wt% CI 0 g/l (2) 10 wt% CI 1 g/l (3) 10 wt% CI 1.5 g/l (4) 10 wtt% CI 2 g/l Coated sample by using epoxy with corrosion inhibitor

3.5 Loaded HNT Experiment (Characterization Tools)

3.5.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate.

Thermogravimetric analysis (TGA) of the raw HNT, thyme oil-loaded HNT, was performed using SDT Q600 (TA Instrument,Melbourne, Australia) under nitrogen flow. The measurements were carried out by heating from room temperature to 900 °C with a heating rate of 20 °C/min[17].

3.5.2 Corrosive solution

A 3.5% NaCl solution obtained by diluting concentrated acid NaCl powder with 100 mL de-ionize water. The environment is not deuterated [21]

3.6 Effectiveness Experimental Procedure (Green Inhibitor Injection and Coating Performance Measurement)

Autolab potentiostat/galvanostat instrument was used for the electrochemical testing. Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR) experiments were conducted using a three-electrode cell with an Ag/AgCl as the reference electrode, the sample as the working electrode, and the stainless steel as the counter electrode or auxiliary electrode. The electrochemical set up in glass cell is as shown in Figure 3.9. The amplitude and the frequency for EIS test were set at 10 mV and 10 mHz to 100 kHz, respectively. Besides, LPR test was carried out by polarising the samples from +10 mV to -10 mV with respect to Ecorr at the scanning rate of 1 mV/s.

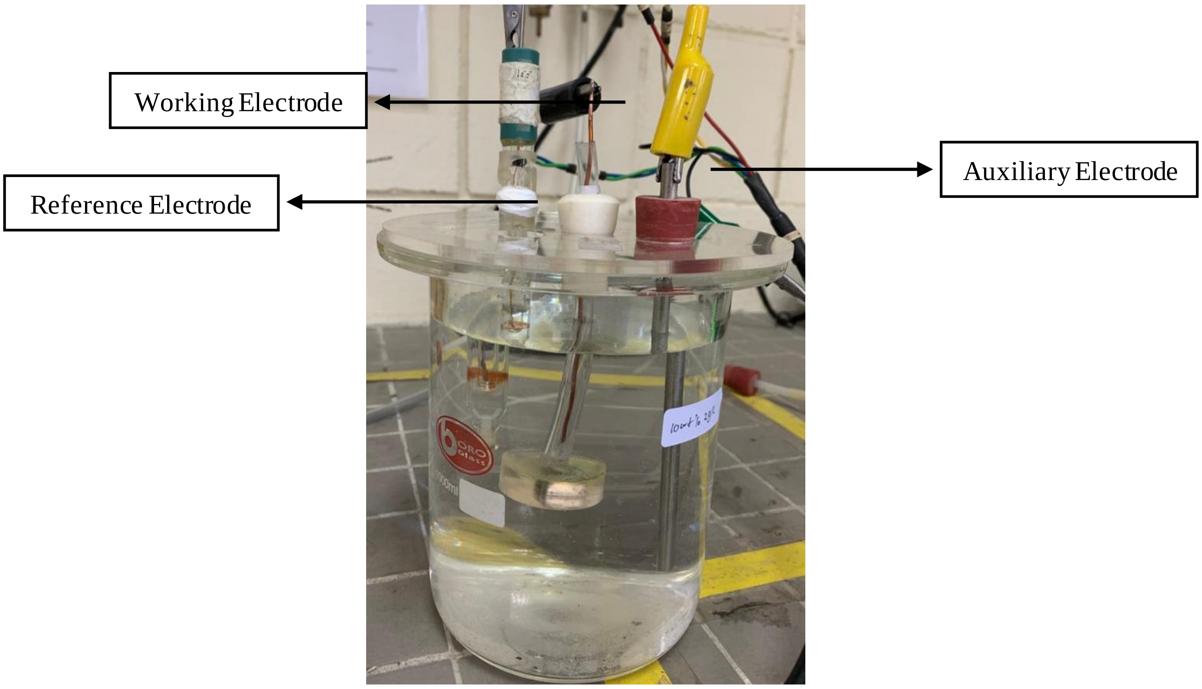


FIGURE 16. Glass Cell Set Up for Electrochemical Testing

3.6.1 Green Inhibitor Injection and Coating Performance Testing

The green inhibitor injection and coating performances of all coated systems were evaluated through visual inspection and electrochemical testing of the immersed samples. All samples were immersed in 3.5 wt% NaCl. Electrochemical testing was conducted to evaluate based on the resistance value of the effectiveness of green inhibitor injection and coating systems, while the visual inspection was conducted to evaluate the coating failure and the adhesion properties after immersion.

3.6.2 Electrochemical Testing

Each cycle of experiment which are as follows [23] :

The set up for the electrochemical test was similar to the set up for the corrosion inhibitor evaluation, as shown in Figure 3.9. In this test, the coated samples were immersed for 24 days in 3.5 wt% NaC. Electrochemical Impedance Spectroscopy (EIS) was conducted as the electrochemical test because it can measure the electrochemical behaviour and the characteristic of charge transfer of the coating. EIS measurements were obtained at the initial duration of immersion (1 hour after immersion), followed by 4, 8, 12, 16, 20, and 24 days of immersion.

3.7 Work Schedule

3.7.1 FYP I

Activity		2019 (By week)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review		■	■	■	■	■	■	■	■	■	■	■	■	■	■
Proposal Writing & Submission							■	■							
RPD									■●						
Sample Preparation										■	■	■			
Progress Asessment 2												■●			
Loading of Corrosion Inhibitor In HNT (TGA)													■	■	■
Interim Report 1 Submission															■●
Green Corrosion Inhibitor (Coating) Preparation and Testing	Loaded HNT Performance (FTIR) CAL Lab														
	Coating Performance Analysis (EIS,LPR)														
Coating Performance Analysis (Surface Structure analysis)															
Characterization of Coating (Optimum Condition)															
Data Analysis															
Final Report Writing & Editing															

■ = Process ● = Milestone

3.7.2 FYP II

Activity		2020 (By week)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review		■	■	■	■	■	■	■	■	■	■	■	■	■	
Green Corrosion Inhibitor (Coating) Preparation and Testing	Loaded HNT Performance (FTIR) CAL Lab	■	■	■	■	■	■	■	■	■					
	Coating Performance Analysis (EIS,LPR)	■	■	■	■	■	■	■	■	■					
Progress Report									■	●					
Coating Performance Analysis (Surface Structure analysis)											■				
Characterization of Coating (Optimum Condition)												■			
Data Analysis											■	■	■		
Final Report Writing & Editing														■	
VIVA															■ ●
Amendment and Submission															■ ●

■ = Process ● = Milestone

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents and discusses the results of the experimental work and analysis of green corrosion inhibitor load HNT for corrosion protection of carbon steel. The results are presented according to the chronology of the research methodology that was elaborated is the previous chapter.

4.1 Characterization of Molecular Structure of Green Corrosion Inhibitor

Figure shows the FTIR spectrum of the studied green corrosion inhibitor loaded HNT . The FTIR spectrum contains the characteristic of the green corrosion inhibitor loaded HNT, as listed in the result table 4.1. For the HNT also stated in the table 4.2 for the differentiate between loaded HNT and without loaded HNT.

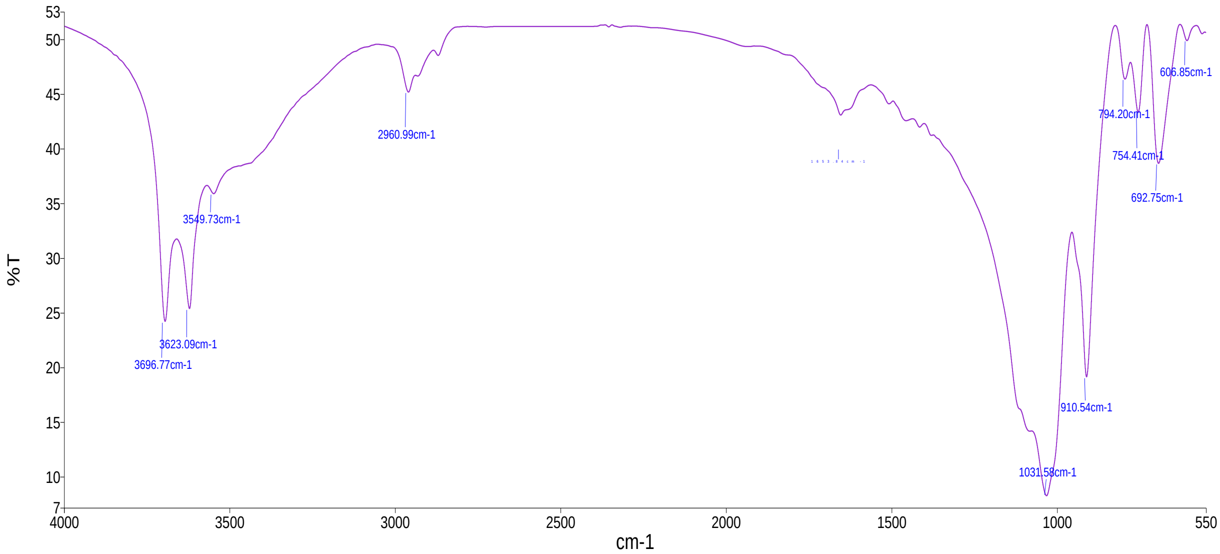


FIGURE 17. FTIR Curve of the 2 g/L Thyme oil Loaded HNT

From the graph above will be translate the wavenumber description of every peaks to show the functional group of inhibited HNT in the table 5 and will be compared with the uninhibited HNT in the table 6 to differentiate the different between the inhibited HNT and uninhibited HNT of the functional group.

TABLE 6. Wavenumber Region for Specific Functional Group Thyme Oil

Wavenumber region	Functional group
3600-3690	O-H stretch of inner surface of hydroxyl group (Al-OH)
Around 3300	O-H stretch
Around 3000	C-H stretch
Around 2900	C-H stretching vibrations specific to CH_3 and CH_2
Around 1600	O-H deformation of water
1600-1700	C=O stretching vibration, C-N stitching, COO- antisymmetric streching
Around 1000	C-O stretch
Around 900	O-H deformation of inner hydroxyl group
Around 790	C-H out of plane bending vibration from isoprenoids
Around 690	CH3-S- (C-S stretch)
Around 600	Disulfides (C-S stretch)

TABLE 7. Wavenumber Region for Specific Functional Group of HNT [26]

Wavenumber region	Functional group
3600-3690	O-H stretch of inner surface of hydroxyl group (Al-OH)
Around 1600	O-H deformation of water
Around 1000	Si-O stretch
Around 900	O-H deformation of inner hydroxyl group
Around 790	Si-O symmetric stretching
Around 690	Si-O stretch

Based on the chemical structure of thyme oil[24], the functional group encompasses C-H stretch, C=H stretch, C-O stretch , C-S strech and O-H 51 stretch of water from the trihydrate content. The peak of O-H stretching for water from the trihydrate content was observed around 3300 cm-1. The peaks around 3000 cm-1, which were 3696.77, 3623.09 and 3549.73 cm-1 are related to O-H stretching. The C-H stretching was represented by 2960.99 cm-1 peak. The peaks that corresponded to partly double bonds of C=O occurred at 1031.58 cm-1. The peaks related to O-H deformation of inner hydroxyl group at 910.54 cm-1. The peak related to C-H out of plane bending vibration from isoprenoids at 794.09, 754.65 cm-1. The peak related to CH3-S- (C-S stretch) at 693.35 cm-1. The peak disulphides (C-S stretch) at 606.72 cm-1. From the FTIR result, it can be concluded that the functional group belongs to thyme oil in the Thyme Oil-loaded HNT, proven by the presence of thyme oil in that molecule.

4.2 Injection Green Corrosion Inhibitor Characterization by EIS

The effect of injection inhibitor in different concentration on the inhibition mechanism can be observed from the EIS impedance plots in Figure 4.4. Increase in inhibitor concentration has led to increase in impedance of the system, which reflects the retardation of the corrosion process. As the impedance value mirrors the protectiveness of the corrosion inhibitor, it can be suggested that the corrosion decrease with increment in inhibitor concentration.

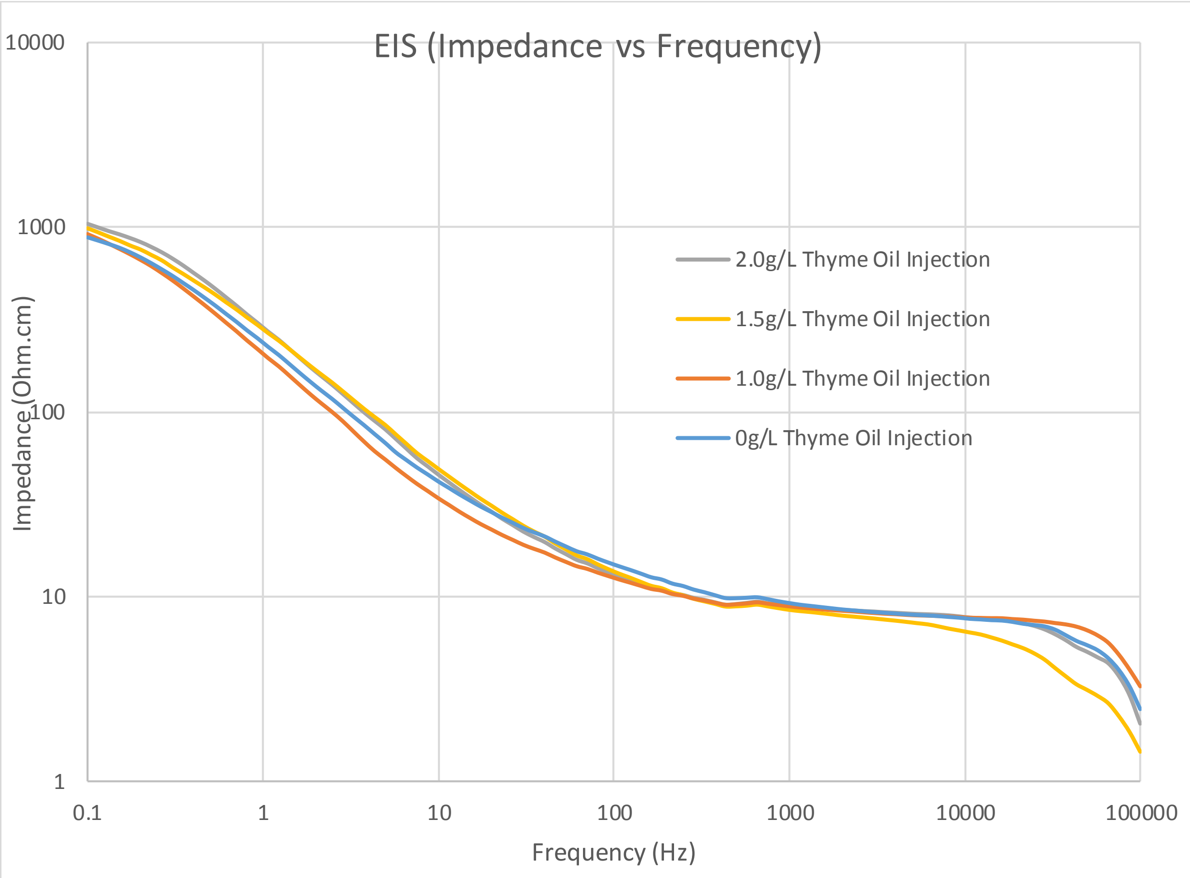


FIGURE 18. EIS plot graph (Impedance Vs Frequency)

In the following sub-sections, the green corrosion inhibitor concentration of 1 g/l, 1.5 g/l and 2 g/l will be characterized in detail with related to the impedances for every concentration of injection during the EIS testing. The graph show that the higher the concentration, the higher the impedance level. As the actual value was be tabulated on table 4.3 for the impedances value at the first touch of graph at 0.1 Hz.

TABLE 8. Value of Impedances for Every Concentration Injection of Thyme Oil

Concentration of Thyme Oil Injection	Impedances (Ohm.cm)
0 g/L	881.84
1 g/L	917.6
1.5 g/L	987.24
2 g/L	1043.1

Figure 19 shows the Nyquist plot of the different test concentration .From figure 19, it can be seen that the impedance increases (last spot of z' value) with injection of inhibitor where as shown in the z' value which is the Nyquist show the real part of the impedance, as the concentration of the thyme oil increase. This confirms the inhibition performance of thyme oil as green corrosion inhibitor.

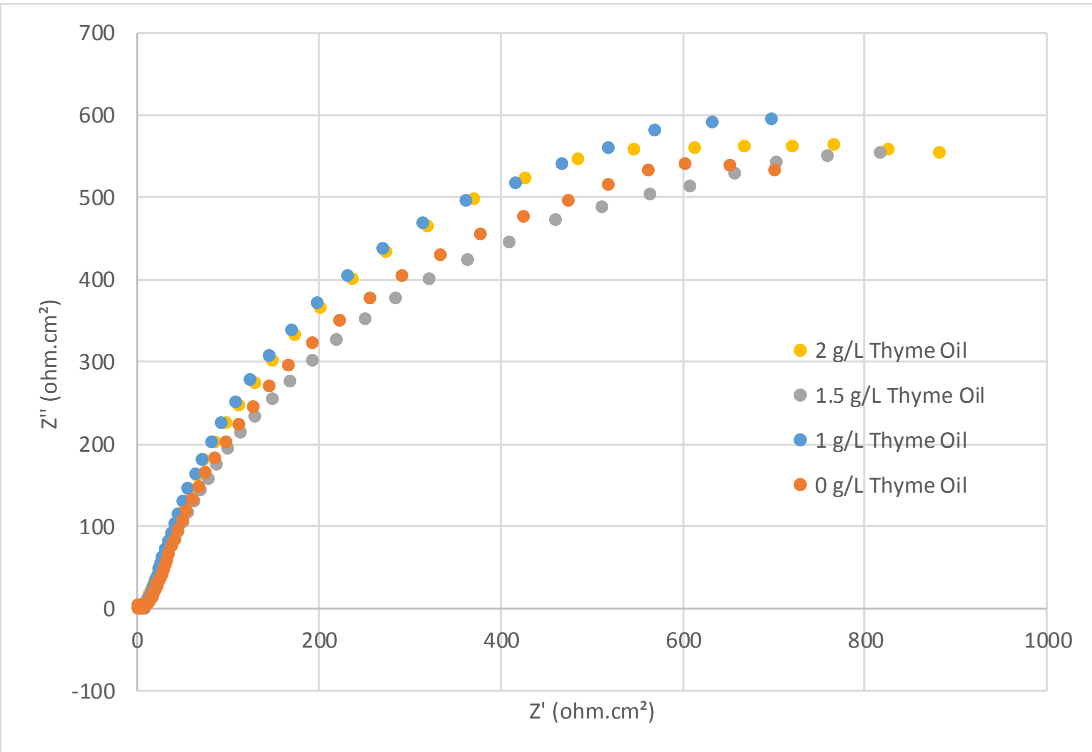


FIGURE 19 : Nyquist plot of uninhibited and inhibited test

4.3 Injection Green Corrosion Inhibitor Characterization by LPR

From figure 20, 21 and 22 it can be seen that the polarization resistance Rt increases with injection of thyme oil which proves the inhibition performance of thyme oil as good green corrosion inhibitor. The polarization resistance Rt of inhibited test solution steadily increases with time.

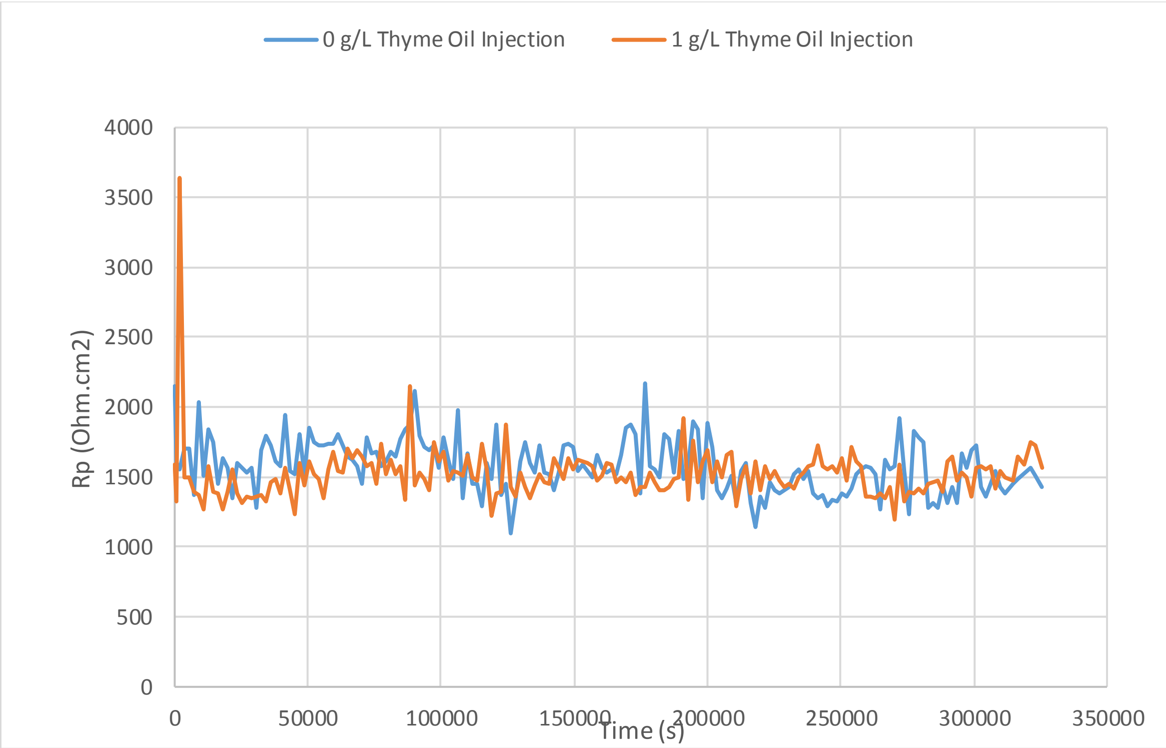


FIGURE 20. Polarization resistance vs immersion time

Inhibition efficiency of thyme oil injection 1 g/L to solution test.

Rp0 = 1429.1
Rp(inh) = 1568.1

$$\text{Inhibition Efficiency} = \frac{Rp(inh) - Rp0}{Rp(inh)}$$

$$\text{Inhibition Efficiency} = \frac{1568.1 - 1429.1}{1568.1} \times 100 = 8.86\ \%$$

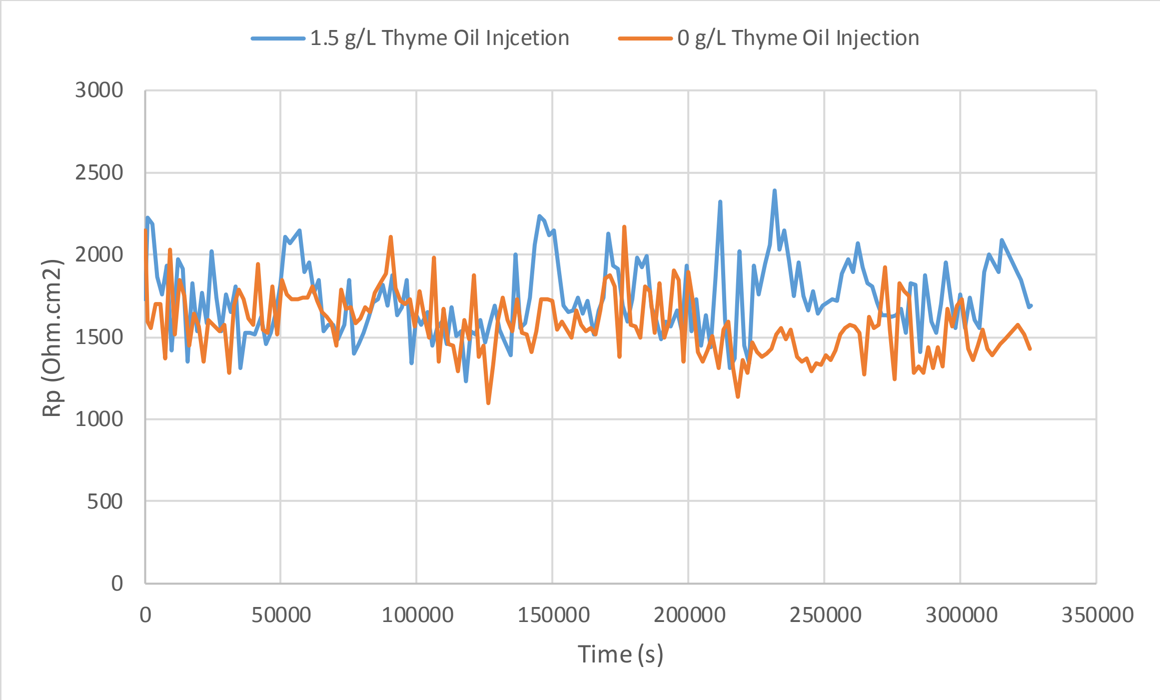


FIGURE 21. Polarization resistance vs immersion time

Inhibition efficiency of thyme oil injection 1.5 g/L to solution test.

Rp0 = 1429.1
Rp(inh) = 1694.4

$$\text{Inhibition Efficiency} = \frac{Rp(inh) - Rp0}{Rp(inh)}$$

$$\text{Inhibition Efficiency} = \frac{1694.4 - 1429.1}{1694.4} \times 100 = 15.66\ \%$$

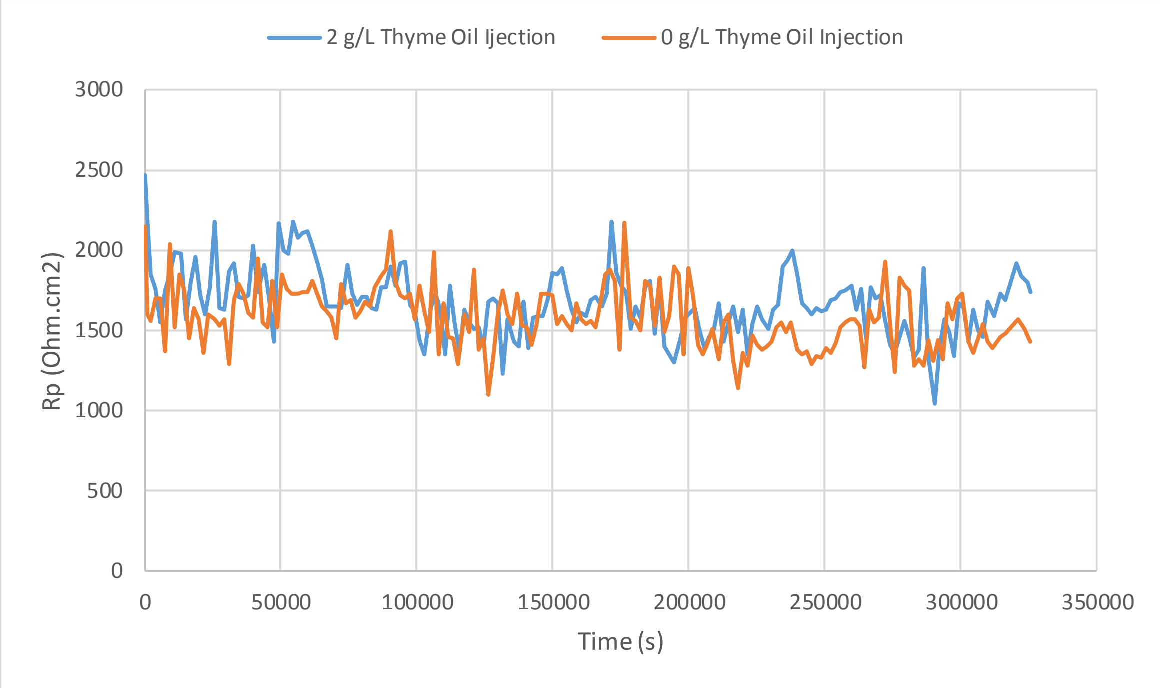


FIGURE 22. Polarization resistance vs immersion time

Inhibition efficiency of thyme oil injection 2 g/L to solution test.

Rp0 = 1429.1
Rp(inh) = 1736.5

$$\text{Inhibition Efficiency} = \frac{Rp(inh) - Rp0}{Rp(inh)}$$

$$\text{Inhibition Efficiency} = \frac{1736.5 - 1429.1}{1736.5} \times 100 = 17.70\ \%$$

The result of LPR test show that the increment of inhibitor efficiency as per increasing concentration of the injection of thyme oil into the solution test. However the result do not show the real characteristic of green corrosion inhibitor because the highest percentage of efficiency only 17.70%. This is because the thyme oil have lower density than the test solution which is 3.5% NaCl. Therefore the green corrosion inhibitor not mix well with the test solution to show the potential of thyme oil as good corrosion inhibitor. Therefore the thyme oil would be loaded into HNT and made as coating on the surface of the specimen with the epoxy.

4.3 Coating of Green Corrosion Inhibitor Characterization by EIS

The effect of injection inhibitor in different concentration on the inhibition mechanism can be observed from the EIS impedance plots in Figure 23. Increase in inhibitor concentration has led to increase in impedance of the system, which reflects the retardation of the corrosion process. As the impedance value mirrors the protectiveness of the corrosion inhibitor, it can be suggested that the corrosion decrease with increment in inhibitor concentration.

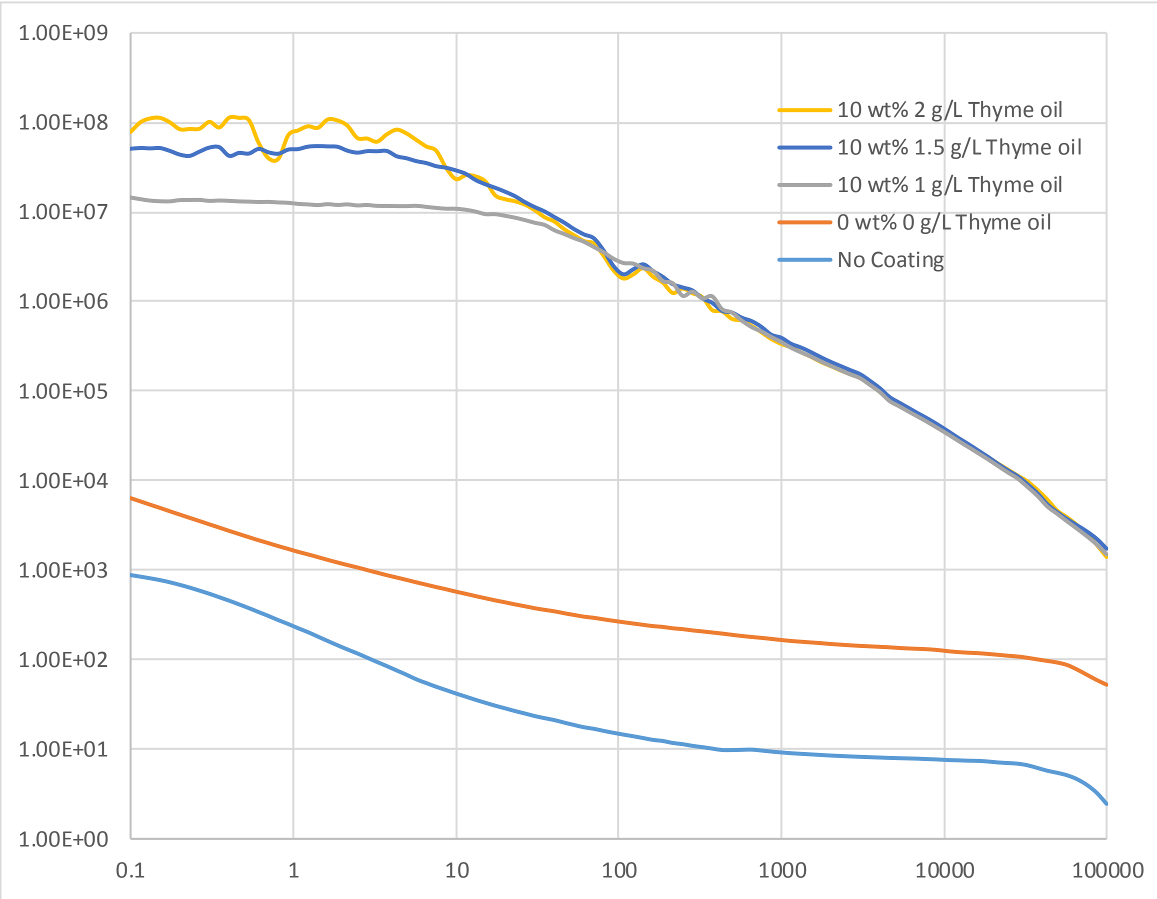


FIGURE 23. EIS plot graph (Impedance Vs Frequency)

In the following sub-sections, the coating of different inhibitor concentration of 1 g/l, 1.5 g/l and 2 g/l will be characterized in detail with related to the impedances for every coating concentration of thyme oil during the EIS testing. The graph show that the higher the concentration of thyme oil in the coating, the higher the impedance level. As the actual value was be tabulated on Table 9.

TABLE 9. Value of Impedances for Every Coating of Concentration Thyme Oil

Coating of Concentration Thyme Oil	Impedances (Ohm.cm)
0 g/L	6378.5
1 g/L	14500000
1.5 g/L	50820000
2 g/L	78300000

Figure 24, 25, 26 and 27 shows the Nyquist plot of the test solution. It can be seen that the impedance increases with coating concentration of green corrosion inhibitor. This confirms the inhibition performance of thyme oil which takes place through adsorption is better by using coating rather by using direct injection.

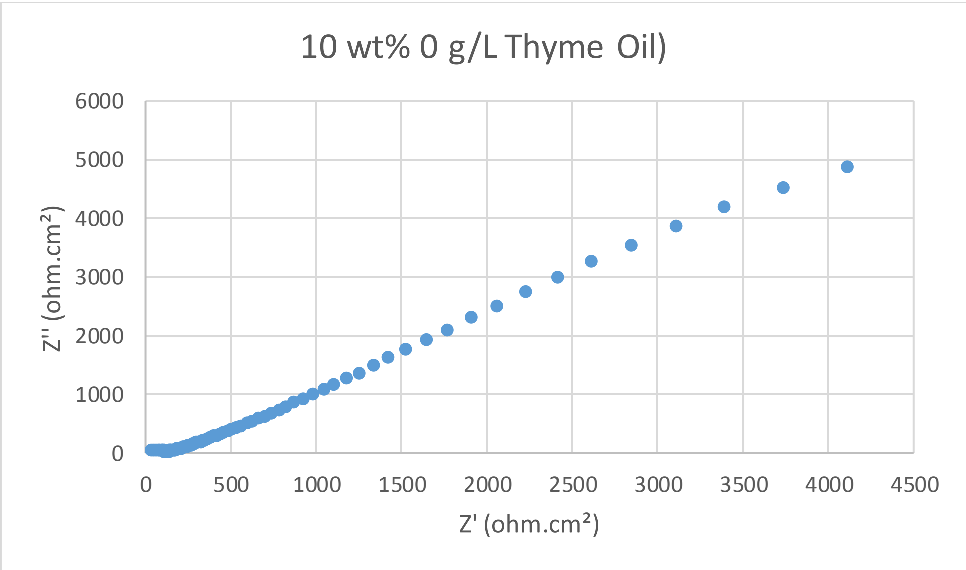


FIGURE 24. Nyquist plot of uninhibited

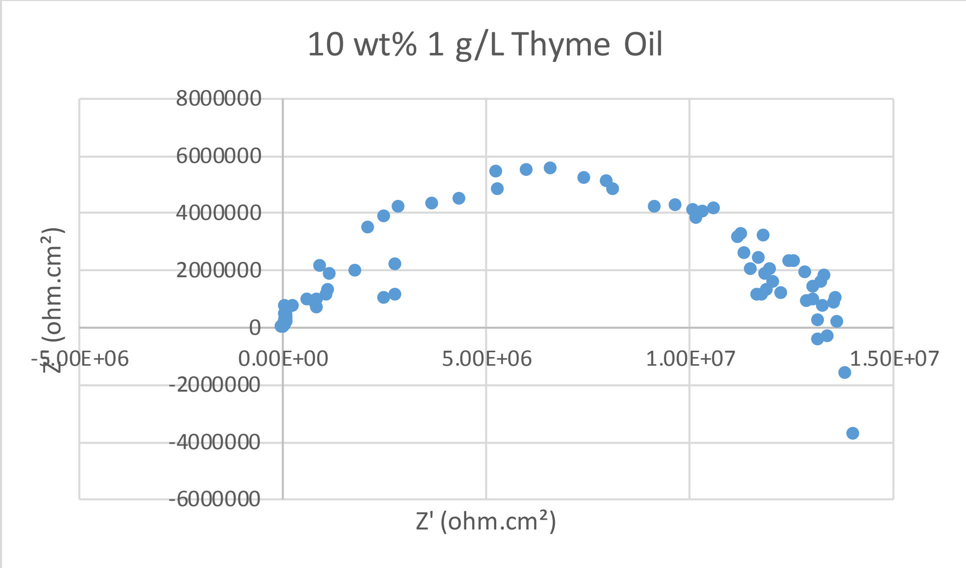


FIGURE 25. Nyquist plot of uninhibited coating and inhibited coating test

Inhibition efficiency of coated inhibited 1 g/L thyme oil loaded HNT.

CR unhibited = 0.00751

CR inhibited = 0.0000214

$$Inhibition\ Efficiency = \frac{CR\ unhibited - CR\ inhibited}{CR\ unhibited}$$

$$Inhibition\ Efficiency = \frac{0.00751 - 0.0000214}{0.00751} \times 100 = 99\%$$

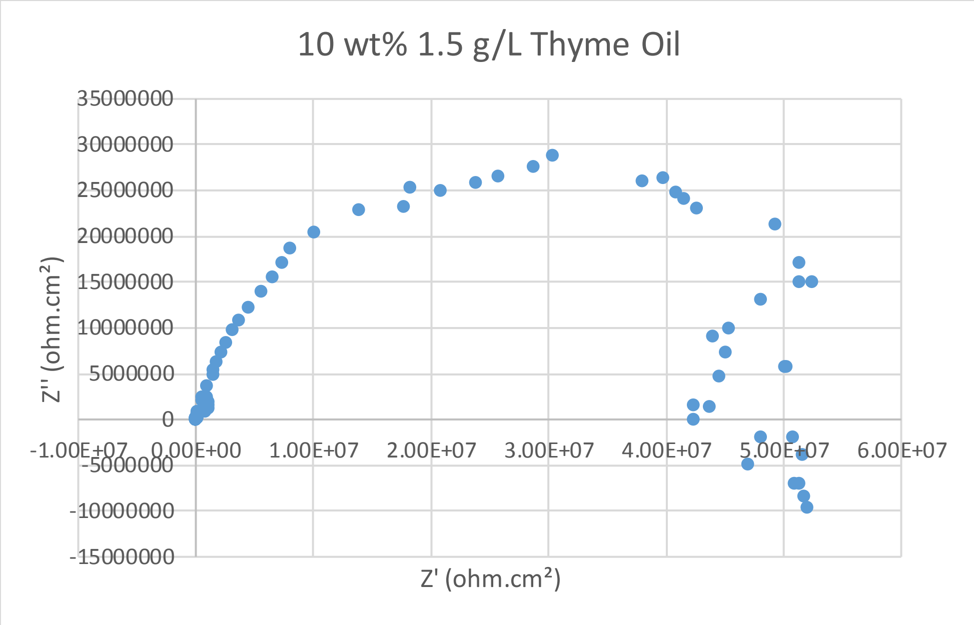


FIGURE 26. Nyquist plot of uninhibited coating and inhibited coating test

Inhibition efficiency of coated inhibited 1.5 g/L thyme oil loaded HNT.

CR unhibited = 0.00751

CR inhibited = 0.00000494

$$Inhibition\ Efficiency = \frac{CR\ unhibited - CR\ inhibited}{CR\ unhibited}$$

$$Inhibition\ Efficiency = \frac{0.00751 - 0.00000494}{0.00751} \times 100 = 99.93\%$$

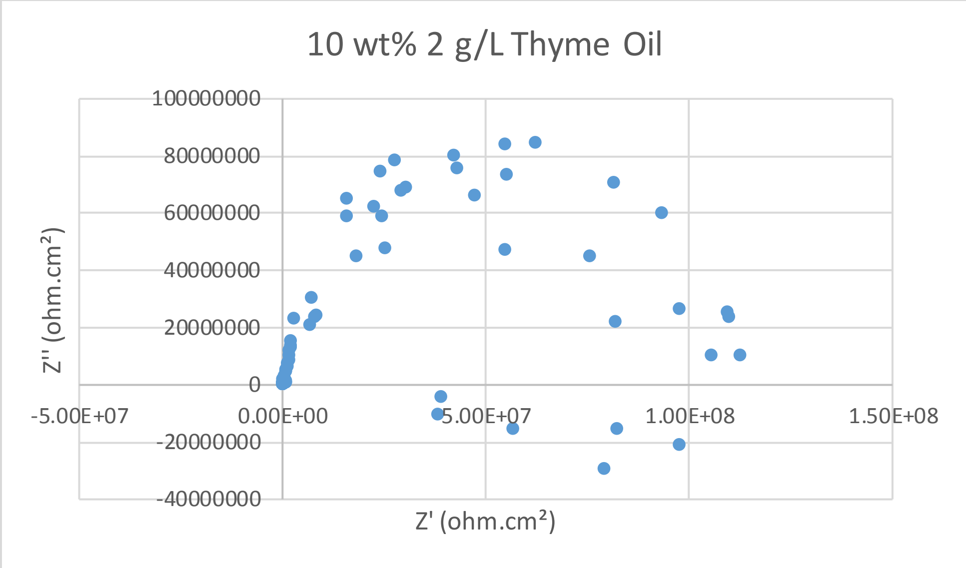


FIGURE 27. Nyquist plot of uninhibited coating and inhibited coating test

Inhibition efficiency of coated inhibited 2 g/L thyme oil loaded HNT.

CR unhibited = 0.00751

CR inhibited = 0.0000027

$$Inhibition\ Efficiency = \frac{CR\ unhibited - CR\ inhibited}{CR\ unhibited}$$

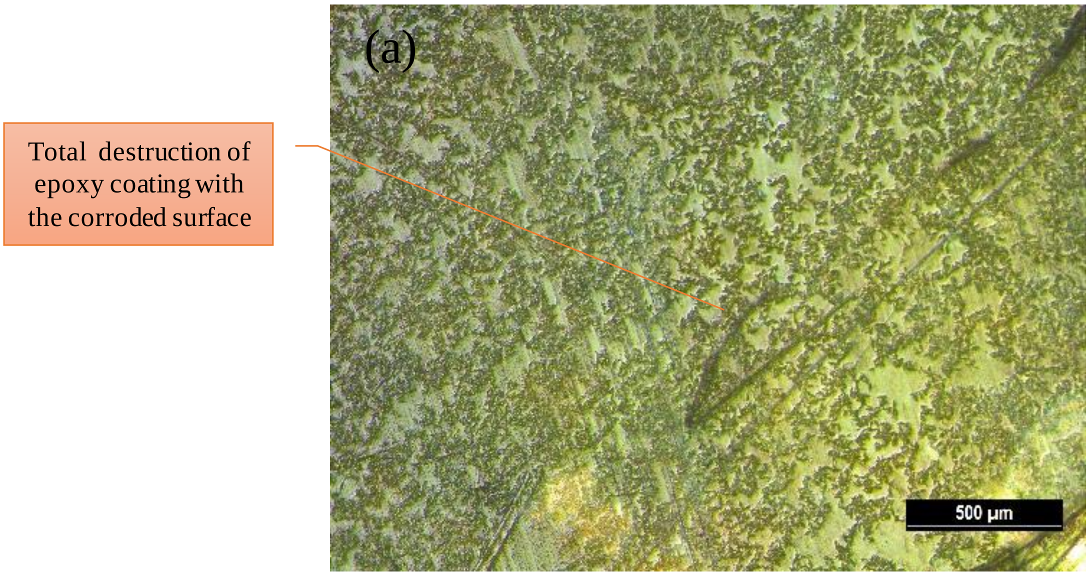
$$Inhibition\ Efficiency = \frac{0.00751 - 0.0000027}{0.00751} \times 100 = 99.96\%$$

The result show the efficiency of green corrosion inhibitor increasing in the coating application as increasing in the concentration of the thyme oil. The highest result show that the coated inhibited with 2 g/L thyme oil loaded HNT with 99.96%. This prove that the application of thyme oil as green corrosion inhibitor loaded HNT in the coating were very good and achieve the performance as the good inhibitor.

4.4 Surface Analysis on The Coated Surface

The electrochemical test for coating systems was evaluated by visual inspection and under an optical microscope. All coated samples were immersed in 10 wt% NaCl for 24 days. Figure exhibits the visual observation of specimen with the inhibited coating and uninhibited coating after 24 days, the significant difference at uninhibited coating can be observed. The progress of corrosion process resulted in the overflow of brown rust. The result reveals the poor corrosion protection of uninhibited coating.

Besides, inhibited coating in all concentrations of thyme oil-loaded HNT shows different behaviour with the neat epoxy coating. As can be seen from Figure 28 , there was no visible evidence of corrosion on the coating surface for inhibited coatings for 2 g/L thyme oil concentration. Further investigation could be conducted under an optical microscope.



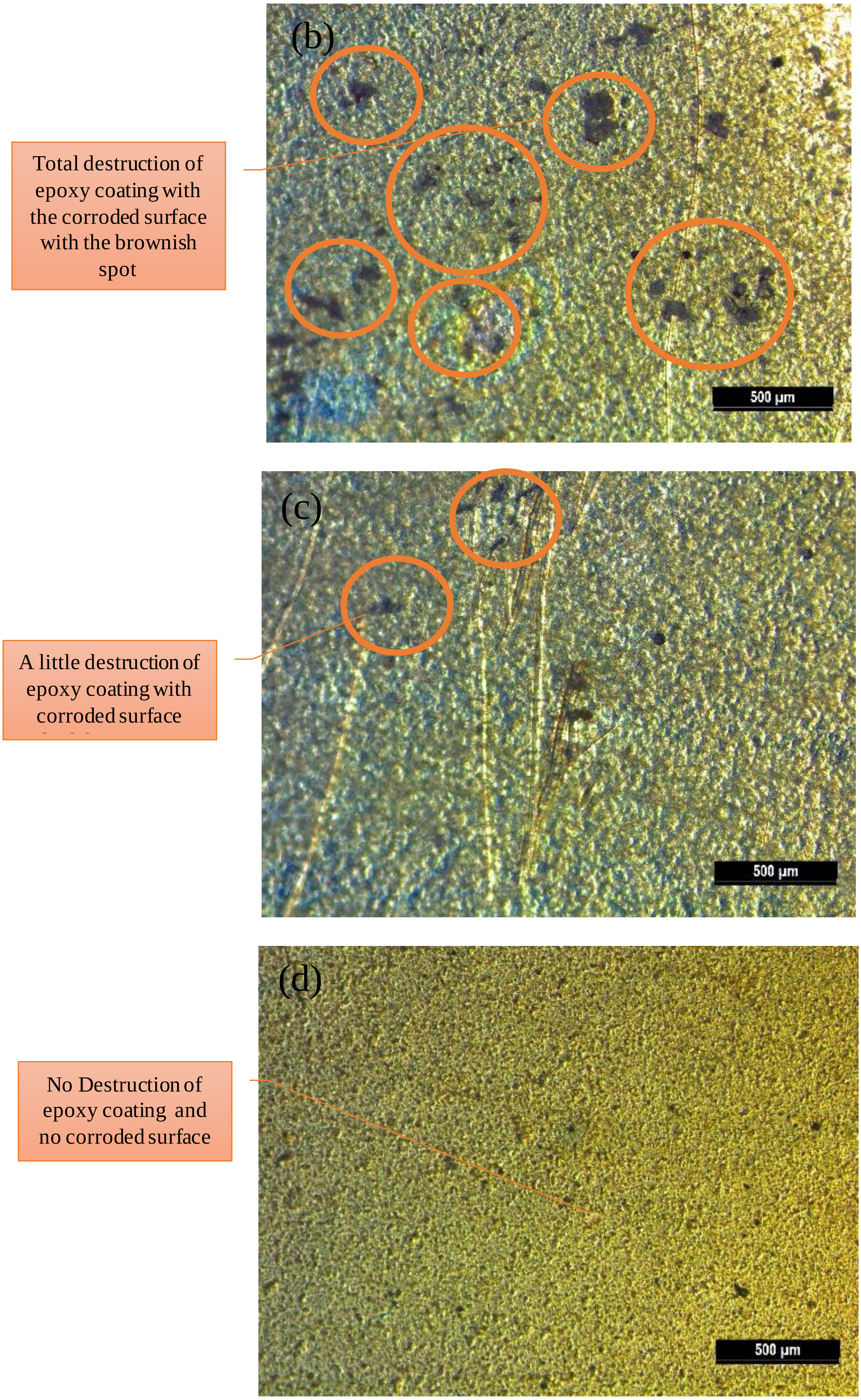


FIGURE 28. (a)(b)(c)(d) Microscopic View For Every Specimen

Further investigations on each coating systems were conducted under optical microscopes which are shown in Figure. For the (a) label which the unhibited coating specimen show the total destruction of the coating and the present of the corrosion all over the surface. Moreover, at (b) which the 10 wt% 1 g/L Thyme Oil Loaded HNT coating and (c) label which is 10 wt% 1.5 g/L Thyme Oil Loaded HNT coating, the brown rust appeared that indicating the corrosion process. Besides, at the (d) label which is 10 wt% 2 g/L Thyme Oil Loaded HNT it can be assumed that corrosion was not occurred due to brown rust did not exist. Moreover, by increasing the concentration of thyme oil-loaded HNT to 10 wt%, the corrosion on carbon steel become decrease. The results revealed that the addition of thyme oil-loaded HNT exhibited better corrosion protection than the neat epoxy. The visual inspections of the scratched defect are in good agreement with the EIS results.

CHAPTER 5

CONCLUSION AND RECCOMENDATION

5.1 Conclusion

Loading of the thyme oil into the HNT as smart coating can be seen in the result of FTIR test where it shows that there is some pick in the graph result. This is show that there is thyme oil successfully load into the HNT. For the electrochemical test, corrosion rates decrease with injection of thyme oil as green corrosion inhibitor, proving that thyme oil acts as good corrosion inhibitor on carbon steel in 3.5% NaCl acidic solution. The different concentration of thyme oil injection which were 1 g/L, 1.5 g/L and 2 g/L purposely to show the different efficiency where the higher the concentration of thyme oil injection the lower the corrosion rate. It also can be seen at the graph where the higher the thyme oil injection, the higher the impedances from the EIS result.

In the inhibition efficiency for injection application test show that the higher the injected green corrosion inhibitor which thyme oil into the test solution, the higher the inhibition efficiency. However, the result of inhibition efficiency is not so good which are 8.86%, 15.77% and 17.70%. Even though the different were not too obvious due to the solution density problem that causes the both corrosion inhibitor and test solution were not mix well between the oil and acidic solution, but the result still show within the presence of the green corrosion inhibitor and uninhibited one.

Therefore the coating application in the green corrosion inhibitor used in this test to show the effectiveness of the coating. From the EIS result show that the higher the concentration thyme oil loaded HNT in the coating, the higher the impedances show in the graph. Inhibition efficiency of coating inhibited with thyme oil were increasing as the concentration of the thyme oil loaded HNT increase in the coating. From the test show that the inhibition efficiency are 99%, 99.93% and 99.96% respectively. From this result also conclude that this green corrosion inhibitor which thyme oil is very compatible and suitable for the coating application where it can show the characteristic and optimize it as corrosion inhibitor.

5.2 Recommendation

The investigation on the inhibited coating with longer time period need to be done for further study to show how the durability and characteristic of the inhibition coating.

Moreover, the additional variables to test inhibited coating under the extreme condition such as the presence of pressure and also varying the working temperature of the product.

Also for the investigation of corrosion inhibitor-loaded halloysite nanotube as an anticorrosive smart coating is recommended for further study. For future work, additional study should be done to develop the self-healing anticorrosive smart coating, such as follows:

Halloysite loaded with a corrosion inhibitor that can be applied to extreme condition or specific condition that can expand the application of the smart coating.

Other nanocontainer that can provide better properties than HNT need to be investigated.

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