MILD STEEL CORROSION INHIBITION BY BLACK TEA EXTRACT IN DYNAMIC SODIUM CHLORIDE SOLUTION

Wan Mohd Norsani Wan Nik[1], Hariz Ariffpudin[1], Nabilah Ismail[2], Mohd Arzaimiruddin Ariffin[3]

[1]Faculty of Ocean Engineering Technology Universiti Malaysia Terengganu, 21300 Kuala Nerus, Terengganu, Malaysia

[2]Faculty of Science and Marine Environment Universiti Malaysia Terengganu, 21300 Kuala Nerus, Terengganu, Malaysia

[3]School of Mechanical Engineering Universiti Teknologi MARA Cawangan Terengganu Kampus Bukit Besi, 23200 Dungun, Terengganu, Malaysia

Corresponding author: *nabilah.i@umt.edu.my*

ABSTRACT

Camellia sinensis (tea) leaves were well-known natural product containing phenolic and flavonoid compounds, which reveals a significant advantage for corrosion inhibition purpose. In this study, the active compound in camellia sinensis (tea) leaves were extracted using several solvents and further characterize with FTIR to identify the functional group in it including their abundance. Corrosion experiment using JR235 mild steel grade with size 25mm x 25mm x 3mm was conducted where these specimens were immersed in the flowing system models in the control condition for 60 days. Corrosion performance was investigate using weight loss method where mild steels were studied and analyzed by using the mathematical equation to determine the weight difference, thus determining the corrosion rate of mild steel plate. In addition, SEM was used in order to monitor the surface morphology of mild steel. Results reveal that corrosive layer formation is being inhibited correspond to extract usage. This research found that the inhibition properties increase with the increasing concentration of extract in sodium chloride solution. Therefore, camellia sinensis (tea) leaves extract serves as an effective and non-toxic corrosion inhibitor for mild steel in dynamic saline condition.

Keywords: corrosion, *camellia sinensis*, spectroscopy, SEM, weight loss

1.   INTRODUCTION

Ships seawater cooling system uses seawater as a medium to cool its heating part of the ship such as the engine, generator and also some of the other appliances. Seawater is an excellent corrosion catalyst especially to the mild steel since the water contains several factors that promotes and speed up corrosion such as low pH and high salinity. So, if there is no counter measure to this problem, the system eventually will corrode, broken and worst case, unusable. To reduce the effect of the corrosion, various methods and procedures need to be conducted and must be taken without any exception since the cooling system of the ship is one of the most important aspects in the ship's system. Mild steel is a good metal especially when it is readily available and costs less than the other metal such as aluminium and titanium [1]. The downside of it is that it corrodes faster than the other metal.

The corrosion inhibitors that has been used widely these days in the coolant are sodium chromate and Borax [2]. This compound is commonly used as an additive inside the coolant agent of an engine because of its magnificent properties of corrosion inhibitor. But unfortunately, these substances are highly regarded as a toxic substance [3] since it can possess a fatal effect to the human and powerful oxidizing agent but is high in toxicity if contact with human both on origin or burnt condition [4].

Since people now are aware of the environment, there are several concerns about the usage of corrosion inhibitors that contains the toxic element in its recipe. Toxic corrosion inhibitors such as chromium is carcinogenic which poison to the human health and environment. To cater this problem, scientist and researchers are starting to move on to natural inhibitor since it is abundant and environmentally friendly. The only problem is with how to get a better inhibitor without jeopardizing the quality of the steel itself. This study is to investigate the effect of tea extract as a corrosion inhibitor used in sodium chloride that act as electrolytes on the corrosion rate of cooling system model.

2.0   RESEARCH METHODOLOGY

2.1   Materials

All materials in this experiment were prepared in the laboratory and of analytical grade. 144 pieces of mild steel with 25 mm x 25 mm x 3 mm of JR235 grade specimens, sandpaper, acetone, tea leaves from BOH tea farm located in Malaysia, sodium chloride solution, ferric chloride, lead acetate, Folin-Ciocalteu's reagent, gallic acid, calcium carbonate, hydrochloric acid, and distilled water were used.

2.2   Methods

2.2.1 Preparing of mild steel.

In this experiment carried, 144 pieces of mild steel with 25 mm x 25 mm x 3 mm of JR235 grade specimens were used. The experiments were conducted out in three test system. This coupon was used according to ASTM for EIS, SEM and weight loss test. All specimens were polished and cleaned with sandpaper grit in 200, 400, 800, 1000, 1200 grade to make sure the surface of the specimens is free from the oxide layer. The metal then was rinsed and clean with distilled water and acetone to remove any impurities at the metal surface. The metal coupon was then dried in the desiccators to keep away any moisture. Tea leaves powder will be extracted using acetone.

2.2.2 Preparation of extraction and sodium chloride solution.

The tea leaves were purchased from the store nearby in powder form. The tea leaves used were from BOH tea farm located in Malaysia. The tea powder was immersed in 75% methanol-water solution for 3 days. Then, the mixture was filtered by nylon paper to remove the rough grain of tea leaves before filter again with filter paper for extra filtration. The remaining solution was further extracted and purified with the rotary evaporator to remove the excess solvent. For the sodium chloride solution, about 245g of salt were dissolved in seven liters of distilled water where these are prepared for three systems with the total of 21 liters of water use.

2.2.3 Qualitative analysis for extraction tea leaves.

The confirmation test of compounds presence within the extract was done.

Table 1: Phytochemical screening test

Sample	Test
0.5 mL of tea extract + 1 mL deionized water	Addition of 2 drops of ferric chloride
o.5 mL of tea extract + 1 mL deionized water	Addition of 2 drops ferric chloride
2.0 mL of tea extract	1 mL lead acetate
0.5 mL of tea extract + 1 mL deionized water	Addition of 2 drops of ferric chloride

2.2.4 Quantitative analysis for the extracted tea leaves

2.2.4.1 Determination of total phenolic contents in the tea extracts

The concentration of phenolic in plant extracts will be determined using spectrophotometric method. Methanolic solution of the extract in the concentration of 1 mg/mL will be used in the analysis. The reaction mixture prepares by mixing 0.5 mL of methanolic solution of extract, 2.5 mL of 10% Folin-Ciocalteu's reagent dissolved in water and 2.5 mL 7.5% $NaHCO_3$. Blank will be concomitantly prepared, containing 0.5 mL methanol, 2.5 mL 10% Folin-Ciocalteu's reagent dissolved in water and 2.5 mL of 7.5% of $NaHCO_3$. The samples were thereafter incubated in a thermostat at 45 o C for 45 minutes. Using spectrophotometer at λmax = 765 nm the absorbance can be determined. Triplicate samples will be prepared for each analysis and the mean value of absorbance can be obtained. The same procedure was repeated for the standard solution of gallic acid and the calibration line can be construed [8].

2.2.4.2 Determination of flavonoid concentrations in the tea extracts

The content of flavonoids will be determined based on the absorbance using spectrophotometer at λmax = 415 nm. The samples also will be prepared in triplicate for each analysis and the mean value of absorbance will be obtained. The same procedure will be repeated for the standard solution of rutin and the calibration line can be construed. Based on the measured absorbance, the concentration of flavonoids can be read (mg/mL) on the calibration line; then, the content of flavonoids in extracts will be expressed in terms of rutin equivalent (mg of RU/g of extract) [8].

2.2.4.3 Tannin concentration determination

Using black and green tea leaves, about 10 grams of each tea sample (dries in oven 1 hour at 85°C prior to use) were weighed and 100 mL of distilled water was added into two separate beakers. It was then boiled in for 20 minutes and filter above boiled solution using funnel and filter paper Whatman grade 1. In order to enable the formation of calcium tannate, 2 gram of calcium carbonate ($CaCO_3$) was added and boiled. The precipitate collected was hydrolyzed with 5 mL concentrated HCl (0.25 M). The resulting crystals of tannic acid obtained from both samples were separated out, dried and weighted. Based on the data recorded, the percentage yield of tannin was calculated.

2.2.5 Preparation of the system

A simple flowing water model system with straight and curve flow were made. 14 mm of polyvinyl chloride pipe and 10 cm x 5 cm of pipe cover is used as straight flow while 24 of 90° polyvinyl chloride junction to study the corrosion rate on the junction. The solution was maintained to circulate along with the experiment with the salinity and pH level check thoroughly with multi-parameter.
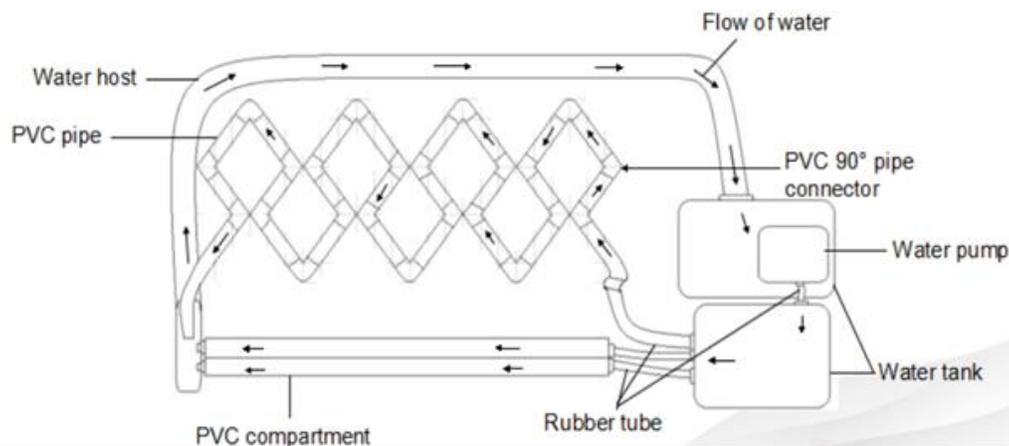

Figure 1: The schematic diagram of the flowing water model system

2.2.5.1 FTIR

Fourier transform infrared devices were used to identify the chemical bonds or the functional group that present in the extract. The tea leaves extract was tested for inhibitor characteristics. Then the result was compared to the other known type of material for further identification.

2.2.5.2 Weight measurement method

This method used to identify the rate of corrosion by the weight difference from the experiment. The initial weight of the specimen was recorded and then at each 10 days interval, the specimen was collected, weight again and the data were collected for 60 days. Equation 1 was used to reevaluate the percentage of the weight difference on the corrosion activity.

$$\textit{Percentage of weight difference}(\%) = \frac{initial\ weight - final\ weight}{total\ weight} \times 100\% \tag{1}$$

2.2.5.3 Scanning electron microscope analysis

18 samples were chosen to be used in the SEM analysis. The samples were observed under the microscope after the end of the experiment to study the morphology of the surface of the mild steel on what has happened on the surface of the steel. The test was conducted in the University Malaysia Terengganu Institute of Oceanography (INOS).

3.0   RESULTS AND DISCUSSION

3.1   Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra graph of the tea leaves was obtained after the test has been conducted as shown in Figure 2. The FTIR was used to identify the chemical bonds and the functional group of the active key components that present in tea extract based on the values of the peak on the graph region.
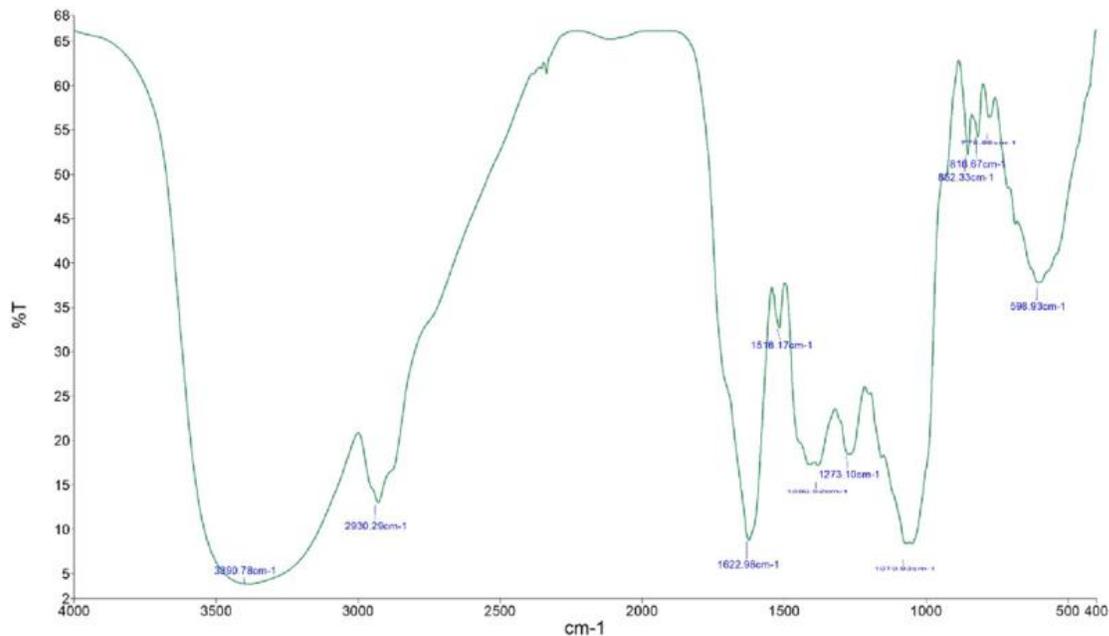

Figure 2: FTIR result for 100% Ethanol extract for Black tea extract

Table 2: IR spectrum of 100% ethanol concentration

Wavelength (cm^{-1})	Interpretation
3391	Phenolic O-H stretching vibration band
2930	Aromatic C-H stretching vibration band
1623	C=C stretching
1273	N-H deformation mode

Based on the spectra obtained for the black tea extract, the absorption band observed were almost similar to the previous study conducted previously. The broad absorption band observed around 3391 cm^{-1} (associated hydroxyl) was overlapped by the strong stretching mode of N-H groups. The aromatic compound was found in region 1800-1600 cm^{-1}. The peak at 1698 cm^{-1} attribute to the presence of C=O attached on the aromatic ring. The peak appeared in the region of 1623 cm^{-1} is due to C=C stretch. The oxygen and nitrogen atoms containing properties of Camellia Sinensis in its functional groups (O-H, N-H, C=C, C=O, C=N) and aromatics rings meets the general consideration of typical corrosion inhibitor [4].

3.2   Qualitative Test

Phytochemical Screening Test

Table 3: The result of phytochemical screening test

Test	Observation	Conclusion
Ferric chloride	Yellow solution changes to blue solution	Presence of gallic tannin
Ferric chloride	Yellow solution changes to green solution	Presence of catecholic tannin
Lead acetate	Yellow solution changes to white solution	Presence of flavonoid
Ferric chloride	Yellow solution changes to blue, red or purple solution	Presence of phenols

3.3   Quantitative Test
3.3.1 Phenolic concentration determination

Graph of Absorbance vs Concentration for Gallic Acid (Phenolic)
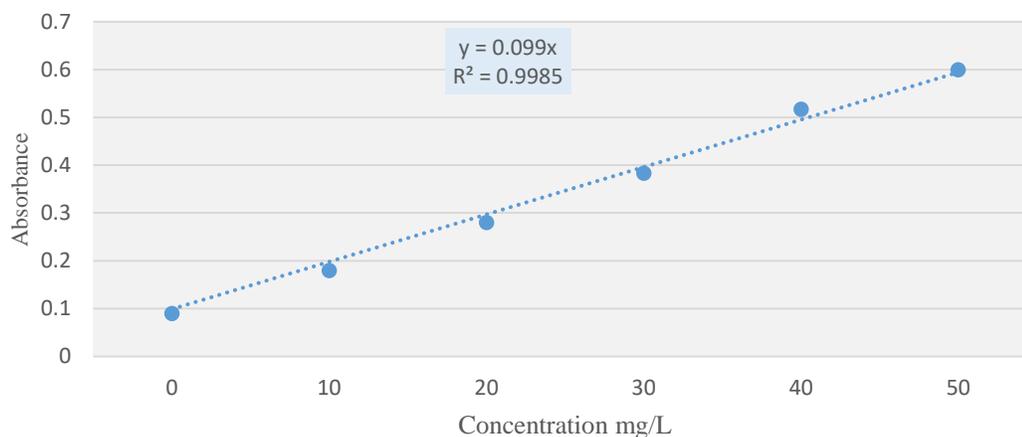
y = 0.099x
R² = 0.9985

Figure 3: Absorbance against gallic acid (phenolic compound) content in black tea extract

The total phenolic contents in the examined plant extracts using the Folin-Ciocalteu's reagent is expressed in terms of gallic acid equivalent (the standard curve equation: $y = 0.099x$, $R^2 = 0.993$). The values obtained for the concentration of total phenols are expressed as mg of GA/L of extract. The total phenolic contents in the examined extracts 5.154 mg GA/L of extract. Hence, the total phenolic content in black tea extract is 8.485 mg/L.
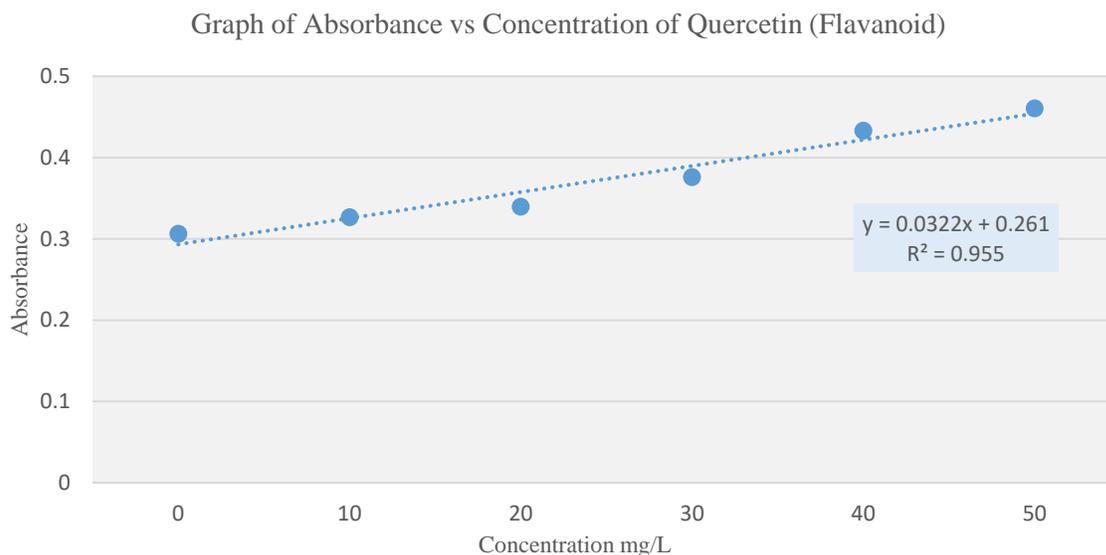
3.3.2 Flavonoid Concentration Determination

Figure 4: Absorbance against quercetin (flavonoid compound) content in black tea extract

The concentration of flavonoids in black tea extract was determined using spectrophotometric method with aluminium chloride. The content of flavonoids was expressed in terms of rutin equivalent (the standard curve equation: $y = 0.0322x + 0.261$, $R^2 = 0.955$), mg of RU/L of extract. The concentration of flavonoids in black tea extract is 1.39 mg/L of extract.

3.3.3 Tannin Concentration Determination

Table 3: Shows the results obtained from tannin concentration determination in black tea leaves

Mass of tea leaves (g)	Mass of tannin acid (g)	Percentage of tannin acid obtained (%)
10.0032	1.3504	13.5

The black and green tea samples were obtained from commercialized Tea BOH. The data collected shows a percentage of tannic acid in black tea. This indicates that black tea would exhibit better inhibition properties. Nevertheless, the production of black tea is higher in Asian and it would apply more to use it as the cost of black tea production is lower.

3.4 Weight Measurement

The calculation percentage of weight gain are analyzed for the rate of corrosion based on the Equation 1. The data that were collected for every 10 days are used to compare the percentage of the additional weight of the steel. Lowest percentage off additional weight at the end of experiment contributes to lower corrosion rate. Figure 5 shows the data percentage for straight flow on concentration stated while figure 6 shows the data for curve flow. The result obtained proved the potential of tea leaves as a potential corrosion inhibitor in sodium chloride solution. After 60 days of immersion, the percentage of additional weight on both 0 mL concentration of tannin is highest compared to specimens immerse in the mix of tea leaves extract on sodium chloride solution. This indicates that the extract of tea leaves can help to protect the steel from rusting.
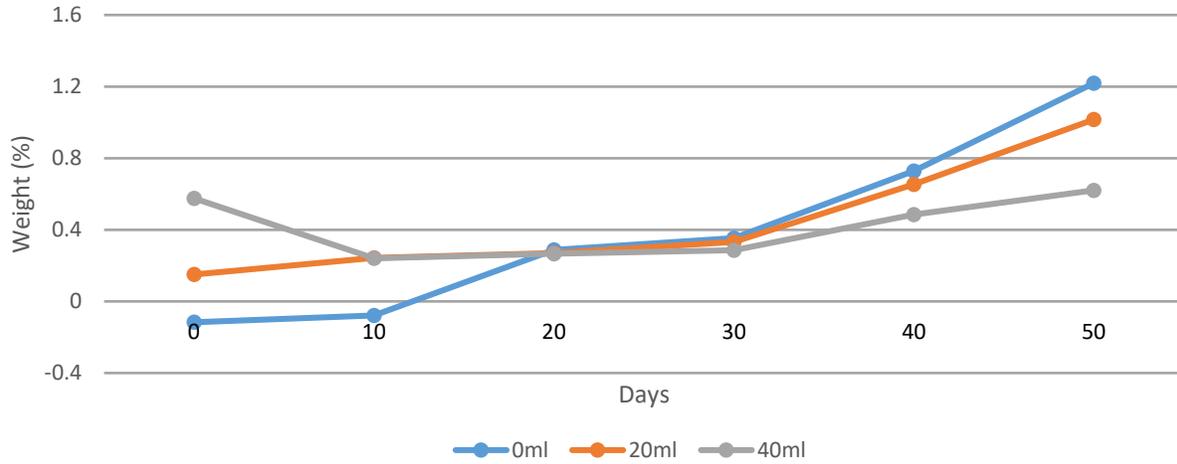
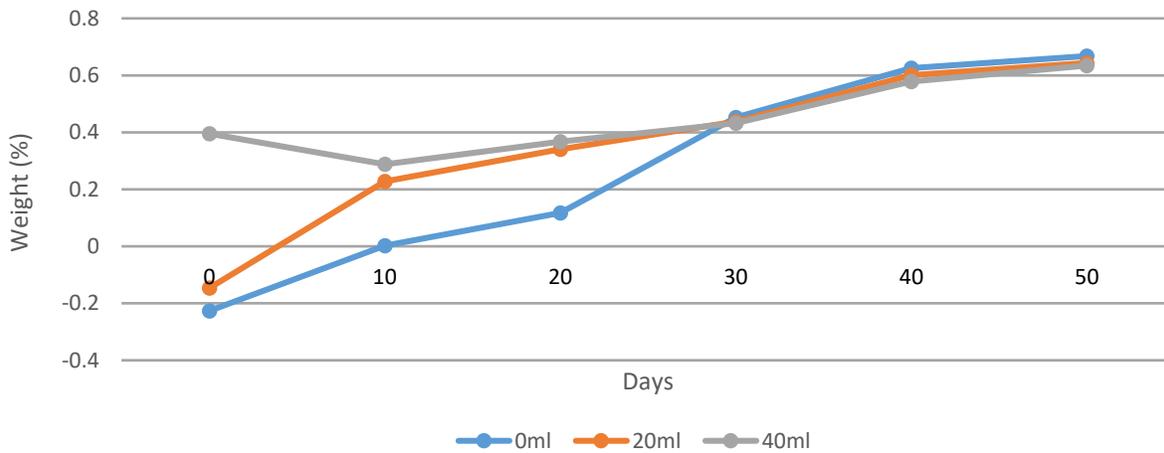*Figure 5: Average weight difference for straight flow*

Figure 6: Average weight difference for curve flow

Data obtained from the weight measurement method was analyzed to obtain and plot the Figure 2 and 3. The graph shows that at the beginning of the experiment, both specimens subjected to tea extract have the highest reading compare to the control specimen, and through the end of the experiment, both manage to gain a lower level of weight compare to control specimen.
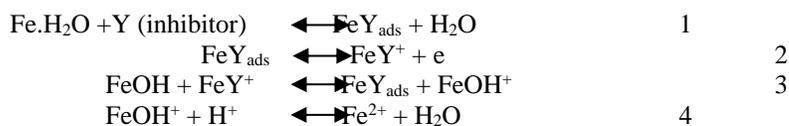
The percentage of weight loss depends on the anodic and cathodic reaction on the mild steel surface.

Anodic Inhibitor

$$Fe^{2+} + Y \text{ (inhibitor)} \longleftrightarrow FeO + OH^-$$
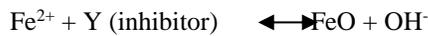
Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. The anodic inhibitor reacts with Fe^{2+} produces insoluble hydroxides which are deposited on the metal surface as insoluble film and impermeable to metallic ion. The result from hydrolysis is hydroxide ions (Dariva and Galio, 2013).

Cathodic Inhibitor

$$Fe.H_2O + Y\ (inhibitor) \longleftrightarrow FeY_{ads} + H_2O \qquad 1$$
$$FeY_{ads} \longleftrightarrow FeY^+ + e \qquad 2$$
$$FeOH + FeY^+ \longleftrightarrow FeY_{ads} + FeOH^+ \qquad 3$$
$$FeOH^+ + H^+ \longleftrightarrow Fe^{2+} + H_2O \qquad 4$$

Cathodic inhibitor function by reducing the available area for the cathodic reaction. This is often achieved by precipitating an insoluble species onto the cathodic sites. The displacement of water molecules on the metal surface yield the adsorbed intermediate FeY_{ads}. It reduces the amount of the species FeOH available for the rate determining step that lead to corrosion. The example of cathodic inhibitors that perform same mechanism are tannins and flavonoid (Dariva and Galio, 2013).

3.5   Scanning Electron Microscope

The specimen of mild steel then was subjected to SEM to observe the surface of the steel after 40 days of the experiment. As from the picture in Table 3 and Table 4, there are several attachments of foreign polyp-like shapes on the surface of the specimen compared to control non subjected with tea leaves extract where common rust shape of cauliflower can be seen.

The highest concentration of tea extract shows the most abundant polyps attach on the surface of the steel. Based on the SEM image shows that the extract reacts with the surface of steel and acts as a temporary layer of protection to the steel itself. This proves why at the beginning of the experiment, both specimens that were subjected to the extract do have higher weight difference compared to the non-subjected specimen.

Table 3: SEM image for straight flow at initial and after 60 days.
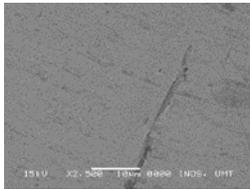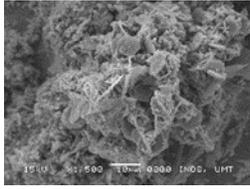
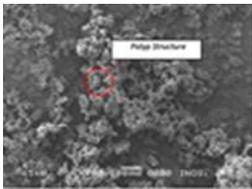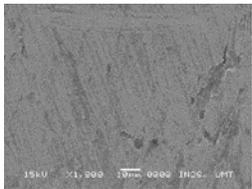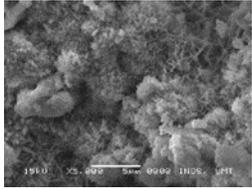| Sample concentration (mL)	SEM image
Initial Image	
0	
20	
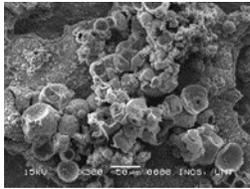
40	

Table 4: SEM imaging for curve flow at initial and after 60 days.
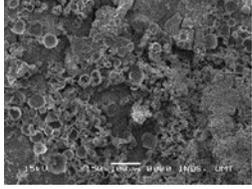
Sample concentration (mL)	SEM image
Initial image	
0	
20	
40	
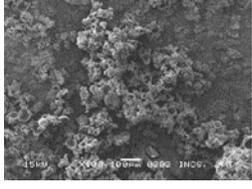
This shows that the inhibitor molecules hinder the dissolution of mild steel by forming surface adsorbed layer of inhibitor and thereby reducing the corrosion rate. It also confirms that the inhibitor effectively controls the corrosion phenomenon by blocking the active corrosion causing sites on the mild steel surface.

3.6   Potentiadynamic Polarization Test

PP test was used to study the effect of corrosion on mild steel by the means of directing the current to the electrode, where the steel coupon with the electrolyte, the salt solution to measure the potential current and rate of the corrosion. AUTOLAB conjoint with NOVA 1.10 software was used to test the steel.

From the potentiodynamic polarization test on model A (0 mL extract), B (20 mL extract) and C (40 mL extract) on straight flow segment, the I_{corr} of C is higher follow by B and A. This shows that the inhibitory action of extract works well on straight flow segment. Rather for the curve flow segment, the A has higher I_{corr} follow by B and C. This result shows that the extract does not react well to attain corrosion from happening since the extract I_{corr} value is lower than the model without any extract introduce.
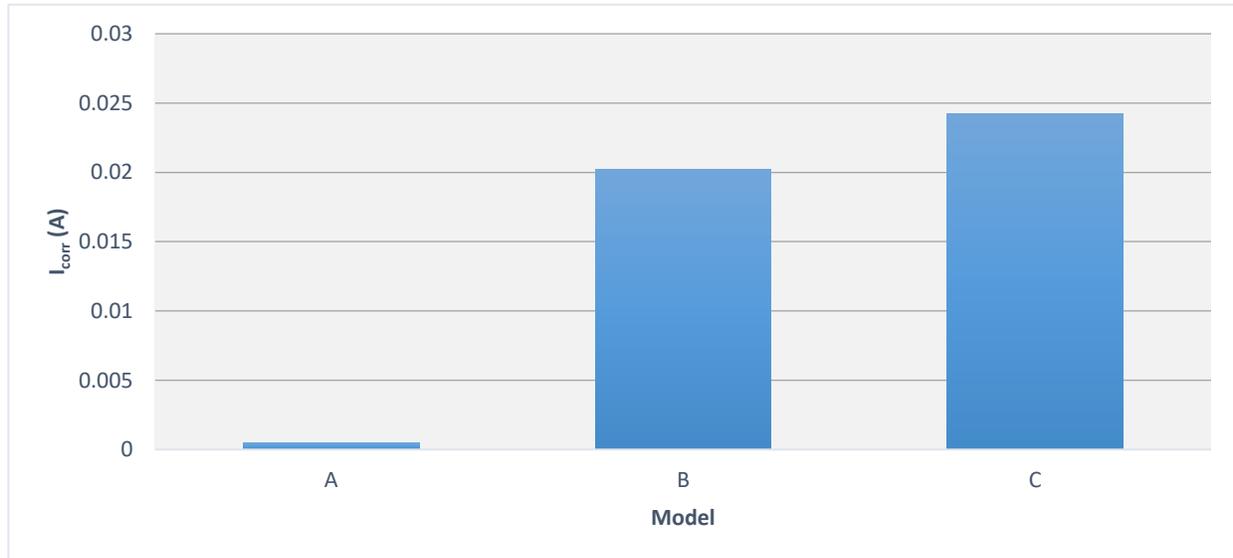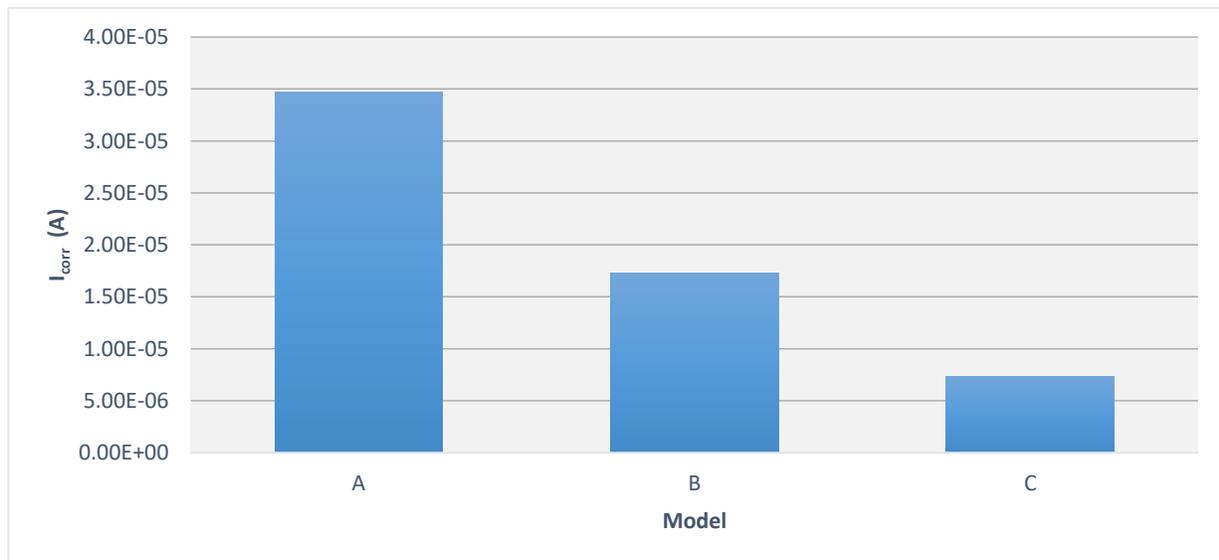

Figure 7: I_{corr} of straight flow segment

Figure 8: I_{corr} graph of curve flow segment

4.　CONCLUSION AND RECOMMENDATION

FTIR has proved that in tea extracts do possess a good inhibiting effect as well as support by weight measurement method towards mild steel in salinity flowing condition. But the effectiveness in inhibiting corrosion depends on the amount of extract used. The results from this test show that a low concentration of extracts can inhibit corrosion especially on the curve section of the pipe where corrosion is usually high. The use of tea leaves extracted as a natural inhibitor can help to reduce the use of harmful inhibitors as well as contribute to a safer environment.

REFRERENCES

[1]　Properties of Mild Steel. (2010). Retrieved from laser-cutting-online: http://www.laser-cutting-online.com/properties-of-mild-steel.htmL

[2]　Cruz, D. R. (2011). Corrosion Inhibitors. Retrieved from Unniversidad Veracruzana: https://www.uv.mx/personal/rorozco/files/2011/02/CORROSION-INHIBITORS.pdf

[3]　Qian, B., Hou, B., & Zheng, M. (2013). The inhibition effect of tannic acid on mild steel corrosion in seawater wet / dry cyclic conditions, 72, 1–9.

[4]　Ramde, T., Rossi, S., & Zanella, C. (2014). Applied Surface Science Inhibition of the Cu65 / Zn35 brass corrosion by natural extract of Camellia sinensis. Applied Surface Science, 307, 209–216. https://doi.org/10.1016/j.apsusc.2014.04.016Sneddon, C. (14 November, 2016). Chormium and its negativity.Retrieved from:http://serc.carleton.edu/NAGTWorkshops/health/case_studies/chromium.htmL

[5]　Nofrizal, S., Rahim, A. A., Saad, B., Bothi Raja, P., Shah, A. M., & Yahya, S. (2012). Elucidation of the corrosion inhibition of mild steel in 1.0 M HCl by catechin monomers from commercial green tea extracts. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 43(4), 1382–1393. https://doi.org/10.1007/s11661-011-1030-3.

[6]　Sheet, C. C. (2015). Sodium Chromate Solution. CAMEO Chemicals

[7]　Dariva, C. and Galio, A. (2013). Corrosion Inhibitors – Principles, Mechanisms and Applications. [Online] pp.367-370. Available at: https://www.intechopen.com/books/developments-in-corrosion-protection/corrosion-inhibitors-principles-mechanisms-and-applications [Accessed 6 Jul. 2018].

[8]　Stankovic, M. S. (2011). Total phenolic content, flavonoid concentration and antioxidant activity of Marrubium peregrinum L. extracts. *Kragujevac J Sci*, *33*(2011), 63-72.