THE EFFECT OF TANNIN ON CARBON STEEL CORROSION IN NITRIC ACID SOLUTIONS

KEEFEKTIFAN TANIN SEBAGAI INHIBITOR KOROSI BAJA KARBON DALAM LARUTAN ASAM NITRAT

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ABSTRAK

Baja karbon merupakan bahan konstruksi yang sering digunakan untuk peralatan proses karena kuat, mudah difabrikasi, dan harganya relatif murah. Namun, baja karbon tidak tahan terhadap korosi oleh fluida proses seperti asam nitrat. Pencegahan korosi peralatan proses oleh asam nitrat dapat dilakukan dengan cara penambahan inhibitor. Salah satu inhibitor yang dapat menurunkan laju korosi baja karbon adalah tanin. Tanin merupakan senyawa organik yang memiliki gugus hidroksil dan karboksil, mudah terurai, tidak beracun, dan dapat menginhibisi korosi baja karbon di dalam larutan asam. Penelitian ini bertujuan untuk menentukan keefektifan tanin sebagai inhibitor korosi baja karbon di dalam larutan asam nitrat, mengetahui mekanisme inhibisi korosi, serta mengetahui dosis tanin yang diperlukan untuk menurunkan laju korosi baja di dalam larutan asam nitrat hingga suatu nilai yang dianggap tidak berbahaya. Penentuan laju korosi dilakukan dengan metoda Tafel, sedangkan mekanisme korosi diprediksi dengan metoda voltametri siklik. Penelitian yang dilakukan bersifat eksperimental, dengan variabel yang dimanipulasi adalah konsentrasi asam nitrat, dosis tanin, dan temperatur operasi. Berdasarkan hasil pengamatan, didapatkan bahwa tanin tidak efektif digunakan sebagai inhibitor korosi baja karbon di dalam larutan asam nitrat. Proses korosi baja di dalam larutan asam nitrat dengan ataupun tanpa tanin berlangsung dalam satu tahap, secara reversibel, membentuk produk korosi yang stabil, dan tidak cenderung pasif. Penambahan tanin sebanyak 80 ppm hanya sedikit menurunkan arus korosi baja di dalam larutan asam nitrat.

Kata kunci: baja karbon, korosi, asam nitrat, inhibitor, tanin

ABSTRACT

Carbon steel is commonly used as construction material of processing equipment due to its strength, ease of fabrication, and low cost. Nevertheless, carbon steel is susceptible to corrosion by process fluid, like nitric acid. However, corrosion effect can be reduced by inhibitor addition. Tannin is one of carbon steel corrosion inhibitors in acidic solution. Tannin is an organic compound which has hidroxyl and carboxyl functional groups, decomposed easily, and non-toxic. The aim of this research is to determine the effectiveness of tannin as a corrosion inhibitor for carbon steel in nitric acid solutions. The corrosion rate is determined using the Tafel method, whereas the corrosion mechanism is predicted by cyclic voltammetry. The results showed that tannin is ineffective to inhibit carbon steel corrosion in nitric acid solution. The carbon steel corrosion reaction in nitric acid solution, with or without tannin addition, is reversible, involving single step oxidation-reduction reaction, resulting stable corrosion product, and not forming any passivation.

Keywords: carbon steel, corrosion, inhibitor, nitric acid, tannin

INTRODUCTION

Carbon steel is commonly used as construction material of processing equipment due to its strength, ease of fabrication, and low cost, but can be easily corroded [3]. Corrosion is the deterioration of metal and metal alloys due to chemical or electrochemical reaction with its environment [13]. Corrosion resulted in decrement of process efficiency, product or environment contamination, loss of raw materials or products, and harmful equipment's damage. Corrosion problem in industry mostly caused by acidic process fluid which is usually used for pickling and descaling, and extreme environment condition [1]. Nitric acid is one of the strongest acid which is often used in industry and can cause corrosion.

Corrosion is unavoidable, but it can be controlled using prevention techniques, such as coating, cathodic protection, or inhibitor (Olasehinde, in [5]). Corrosion inhibitor is a chemical subtance, that when added in a small concentration to an environment, effectively decreases the corrosion rate [13]. It could be made whether from organic or inorganic compound. Some examples of inorganic compound, such as chromate, dichromate, nitrite, and phosphate are used widely as a corrosion inhibitor in many medium (Fontana, in [9]). On the other hand, inorganic corrosion inhibitor such as chromate and several organic inhibitors are biotoxic compound (Hosseini and Azimi, in [9]) and not environmentally friendly, so its used is limited [5]. Therefore, the research and the application of more environmentally friendly, non-toxic, easily obtained, and low cost in large scale corrosion inhibitor was began.

Tannin is an organic compound which can be decomposed easily, non-toxic, and easily obtained. This compound comprise of complex polyphenols and hydroxyl functional groups, which interact with metal ion forming insoluble metal-tannates [10]. Tannin is widely used as paint pigment, rust converter component, and as an oxide descaling in process equipments [12]. Literature study showed that tannin is a good corrosion inhibitor alternative in acidic solution [12], but the quantitative data about the effective dosage of tannin as a corrosion inhibitor for carbon steel in nitric acid is not yet available. Therefore, a research is required to obtain tannin dosage as carbon steel corrosion inhibitor in nitric acid solution.

The aim of this research is to determine the effectiveness of tannin as a corrosion inhibitor for carbon steel in nitric acid solution. While the objectives of this research are to determine the effect of tannin on carbon steel corrosion in nitric acid solution, to understand the mechanism of corrosion inhibition by tannin, and to determine the amount of tannin needed to reduce the corrosion rate of carbon steel in nitric acid solution to a negligible value.

The scopes of this research are:

1. Measurement of carbon steel corrosion rate in nitric acid solution using tannin as an inhibitor, with nitric acid concentration, tannin dosage, and operating temperature as manipulated variables.
2. The determination of corrosion rate was carried out using the Tafel method.
3. The corrosion mechanism is predicted by cyclic voltammetry.

MATERIALS AND METHOD

Carbon steel plate, tannin and nitric acid solutions were used in this experiment. The electrochemical measurements were performed using a potentiostat which is connected to an analytical software installed in a PC, a salt bridge coupled with a reference electrode (saturated calomel), auxiliary electrode (platinum wire), and thermometer.

The scheme of equipments arrangement is shown on Figure 1.

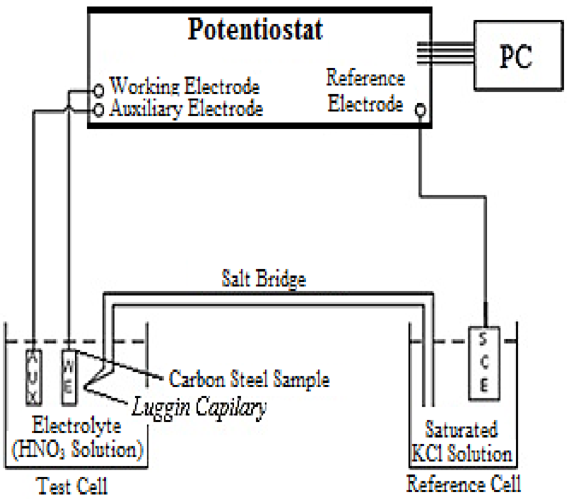

Figure 1. Scheme of Equipments Arrangement for Anodic Polarization Measurement (ASTM G5-82, 1997)

The specimen is made of 1 x 1 cm^2 low carbon steel plate of 2 mm thickness embedded in a cold epoxy resin. The compositions of the low carbon steel plate in mass fraction are 0.13 C; 0.078 Si; 0.018 P; 0.006 S; 0.321 Mn; 0.414 Cu and Fe balance.

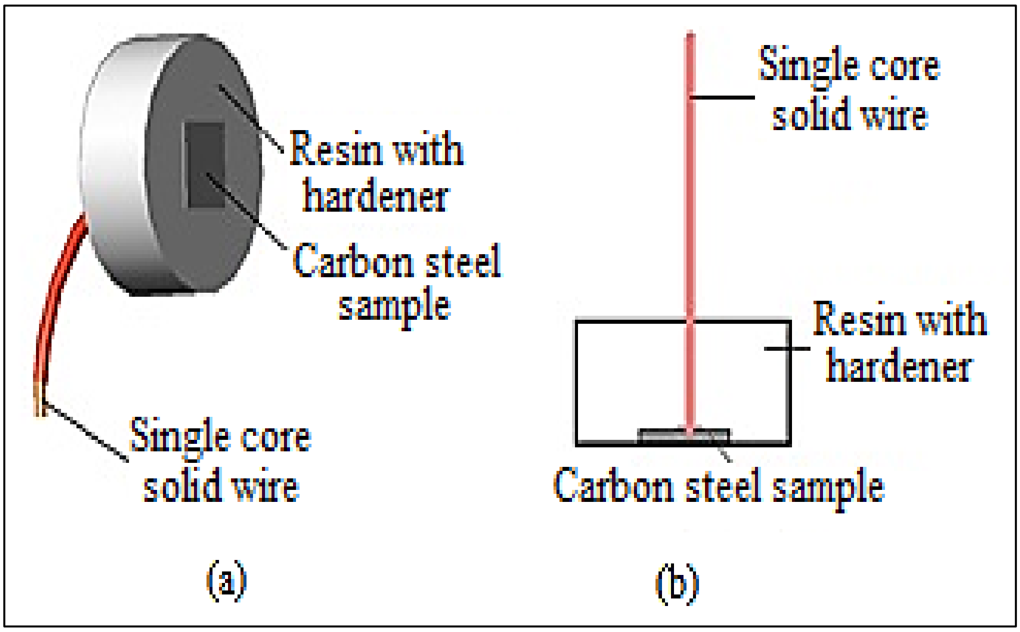

Figure 2. (a) Specimen Photograph (b) Scheme of Specimen Side View

The concentrations of nitric acid solutions used in this research are 0.1 M; 0.2 M; and 0.4 M. Tannin, which was extracted from tea leaf, was used as an organic inhibitor in 20 ppm, 40 ppm, and 80 ppm dosage. Beside of nitric acid concentration and tannin dosage, operating temperature was also varied at 25^{o}C, 40^{o}C, and 60^{o}C.

Assuming that the corrosion attack is uniform, corrosion rate was determined using Tafel method by a polarization curve. This curve represents the relationship of potential and logarithmic of current density. The corrosion current density (icorr) is the abcissca of the intersection of anodic an cathodic curve at corrosion potential (Ecorr) in the polarization curve.

The corrosion rate can be determined using the Faraday formula [6]:

$$\text{Corrosion Rate} = K \times \frac{i_{corr} \times a}{nF} [=] \frac{mm}{year} \qquad (1)$$

Where K is a conversion factor, icorr is the corrosion current density, a is the relative atomic mass, n is the number of electrons involved, and F is the Faraday constant (96500 Coulomb/ equivalent).

Inhibition efficiency of tannin is calculated using this equation.

$$\eta = \frac{CR - CR_i}{CR} \times 100\% \qquad (2)$$

In general, the inhibitor efficiency will increase linearly with the increment of inhibitor concentration. A good inhibitor can decrease the corrosion rate with 90% efficiency when added in 40 ppm, or 95% efficiency when added in 80 ppm [13].

RESULTS AND DISCUSSION

As shown in Figure 3, it is obvious that the corrosion rate of carbon steel decreases linearly with the increment of tannin concentration in 0.2 M nitric acid solution at room temperature. This indicates that tannin can reduce the carbon steel corrosion rate in nitric acid solution.

But tannin is not an effective inhibitor, beacuse its effectivity is only 2.44% when its concentration is 40 ppm, and its effectivity is 28.05% when tannin concentration is 80 ppm. This inhibition capability was not shown if the other manipulated variables were changed.

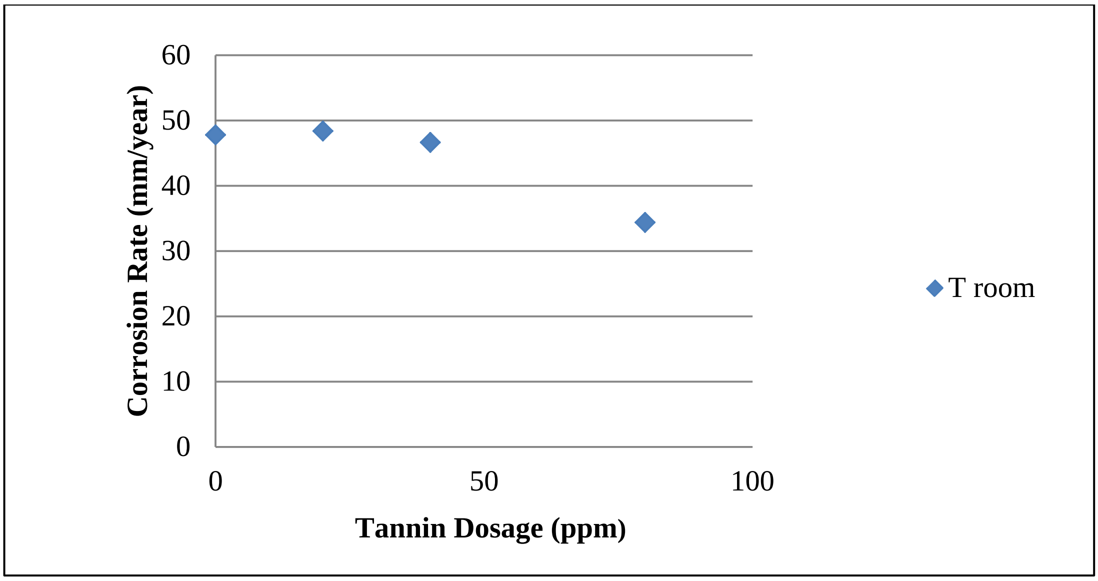

Figure 3. The Corrosion Rate of Carbon Steel with Tannin Addition in 0.2 M Nitric Acid Solution at Room Temperature (25^{o}C-27^{o}C)

The Effect of Nitric Acid Concentration on The Corrosion Rate

Figure 4 shows that the corrosion rate of carbon steel rises with increasing nitric acid concentration from 0.1 M to 0.4 M at room temperature. At higher temperature, carbon steel corrosion rate increases with rising nitric acid concentration from 0.1 to 0.2 M, but decreases with higher nitric acid concentration of 0.4 M. The highest corrosion rate of carbon steel in each nitric acid concentration is found at room temperature. These phenomena might be caused by oxide film formation on the metal surface. As the temperature rises and the oxidizing agent (H^+ and NO_3^- ions) concentration increase in the solution, the more oxide film will be formed and the larger coverage of the metal surface. Therefore the metal will be protected from the oxidizing attack, which resulted the reduction of corrosion rate.

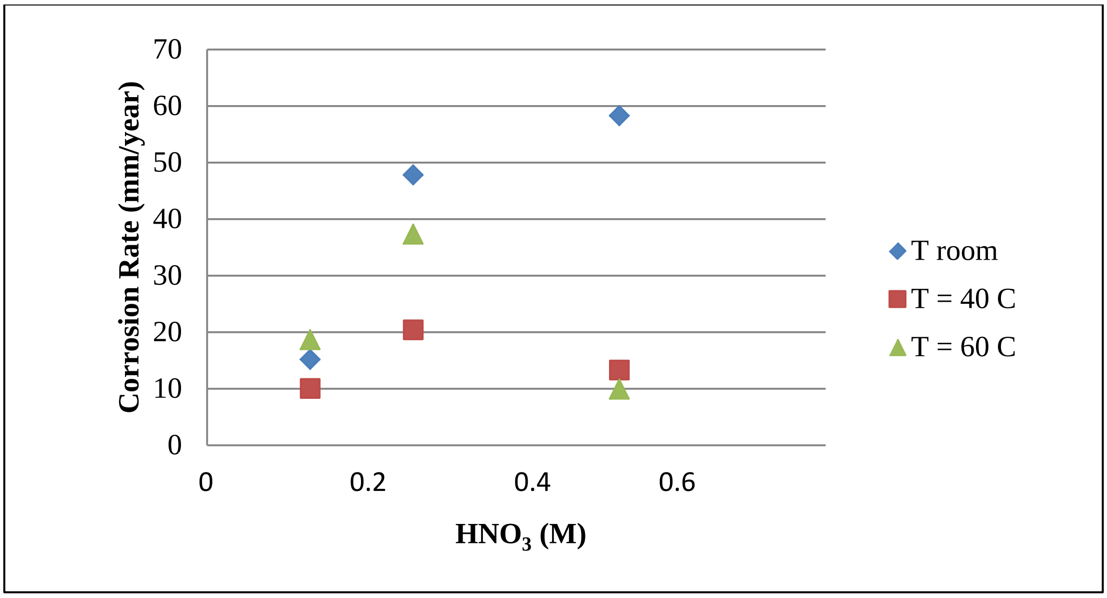

Figure 4. Effect of Nitric Acid Concentration on Carbon Steel Corrosion Rate at Various Temperature without Tannin Addition

The Effect of Tannin Concentration

Figure 5 shows that tannin addition has altered the carbon steel corrosion rate. It also shows that the corrosion rate increases with higher acid concentration. Corrosion rate fluctuation was a result of tannin function as a rust converter. Tannin will react with rust on metal surface producing an unharmful compound [14]. According to NACE [14], tannin is the heart of rust converter compound. Tannin will react with iron oxide, forming ferric tannate, a stable blue-black corrosion product.

The rust conversion reaction occurs chemically, changes porous free iron compound to a more soluble compound. NACE [14] said that, if the amount of the rust converter is insufficient, not all rust will be converted. The leftover rust will be a new starting point for the new corrosion process.

Based on NACE theory [14], the fluctuation of the corrosion rate is caused by an instant attack of NO_3^- and H^+ ions on carbon steel surface when the metal enters the nitric acid solution and form a thick oxide film. Tannin which added into the system, will be gradually bound with the rust (oxide film) on carbon steel surface.

The addition of 20 ppm tannin into nitric acid solution at various concentrations at room temperature, reduces the carbon steel corrosion rate. This fact shows that the amount of tannin added is not sufficient to convert the oxide film.

The addition of 40 ppm tannin into various concentration of nitric acid solutions, has increased carbon steel corrosion rate, even higher than without tannin addition.

This phenomenon might be caused by the higher activity of tannin to convert the metal oxide, compared to the activity of oxide film forming by nitric acid. As the amount of tannin added was not large enough, therefore, not all the iron oxide have been converted, and the leftover iron oxide will be a new starting point for the new corrosion process.

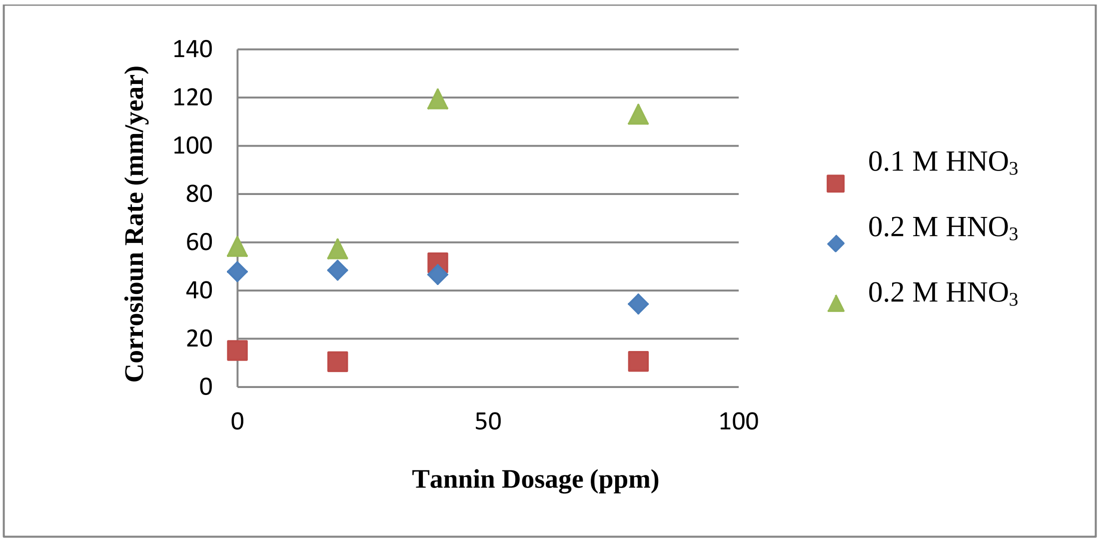

Figure 5. The Effect of Tannin Dosage on Carbon Steel Corrosion Rate in Various Concentration of Nitric Acid Solutions at Room Temperature (25°C-27°C)

Meanwhile, the addition of 80 ppm tannin to various concentration of nitric acid solutions, tend to increase carbon steel corrosion rate, butless than the corrosion rate of 40 ppm tannin addition. This fact shows that 80 ppm tannin is sufficient to convert all of iron oxide film and accelerate corrosion attack, but it does not leave a starting point for a new corrosion process. There is still a possibility that some tannin molecules are bound to the free iron ion (which is not forming iron oxide yet), producing a passive ferric tannate layer on carbon steel surface. Based on the explanation above, it can be concluded that tannin is ineffective as carbon steel corrosion inhibitor in this experiment, because the optimum condition where tannin can form a ferric tannate passive layer is the pH range of 2.0-2.5, whereas the pH of HNO_3 solutions in this experiment are in range of 0.4-1.0 [14].

Effect of Temperature

Figure 6 shows that at 40°C and 60°C, the carbon steel corrosion rate in 0.2 M nitric acid is fluctuated with tannin addition. The corrosion rate that shown in Figure 6 did not follow the Arrhenius theory which stated that the reaction rate will increase with rising temperature, with or without tannin addition.

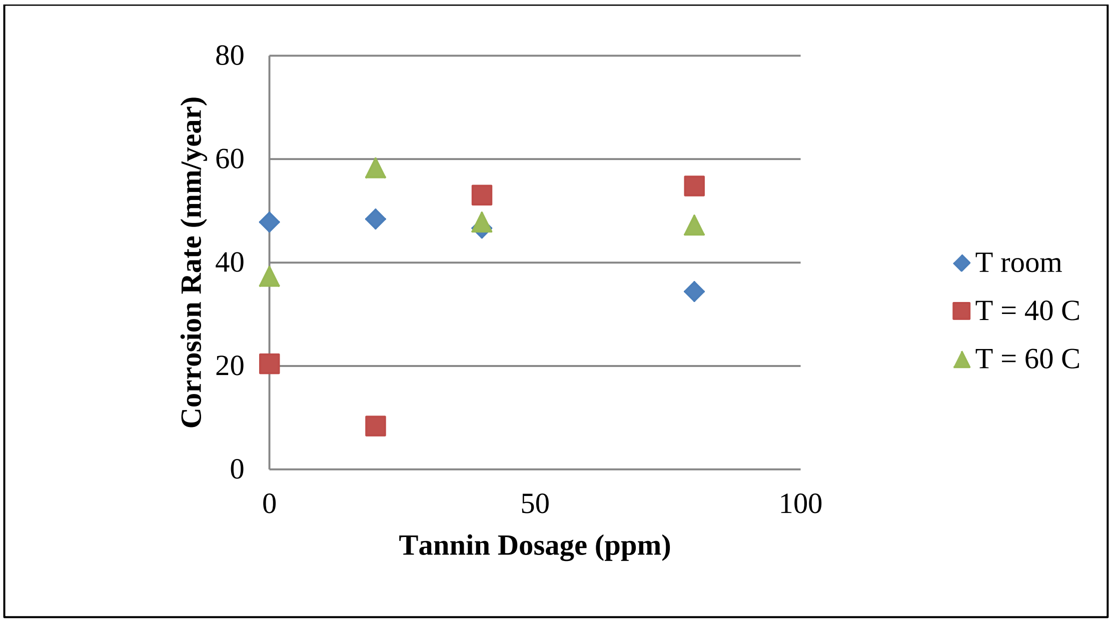

Figure 6. Effect of Tannin Dosage in 0.2 M Nitric Acid Solution at Various Temperature

This fluctuation may be due to independence of nitric acid protonation rate to temperature. The oxidation capacity of nitric acid, therefore, is also independent to temperature.

The addition of 20 ppm tannin into 0.2 M nitric acid solution at 40°C has reduced carbon steel corrosion rate in this solution. This phenomenon shows that at that temperature, tannin is able to form ferric tannate passive layer in collaboration with ferric ions produced by nitric acid corrosion. However, further addition of tannin into the same nitric acid solution has increased the corrosion rate, even more than such without tannin addition. All dosages of tannin addition into 0.2 M nitric acid solution at 60°C have increased carbon steel corrosion rate in this solution. The later phenomena show that at temperature of 40°C and above, tannin has a greater tendency to be a rust converter than a passive film former.

Effective Tannin Dosage

Corrosion rate is considered not harmful if it value is lower than 2 mpy or 0.05 mm/year (NACE in [6]). Tannin dosage that may give a corrosion rate of less than 0.05 mm/year can be obtained from linear extrapolation of tannin concentration as a function of carbon steel corrosion rate as shown in Figure 7, which is equal to 286 ppm. Tannin dosage of 286 ppm is an excessive value, because a good inhibitor is used with concentration of 40-80 ppm [13].

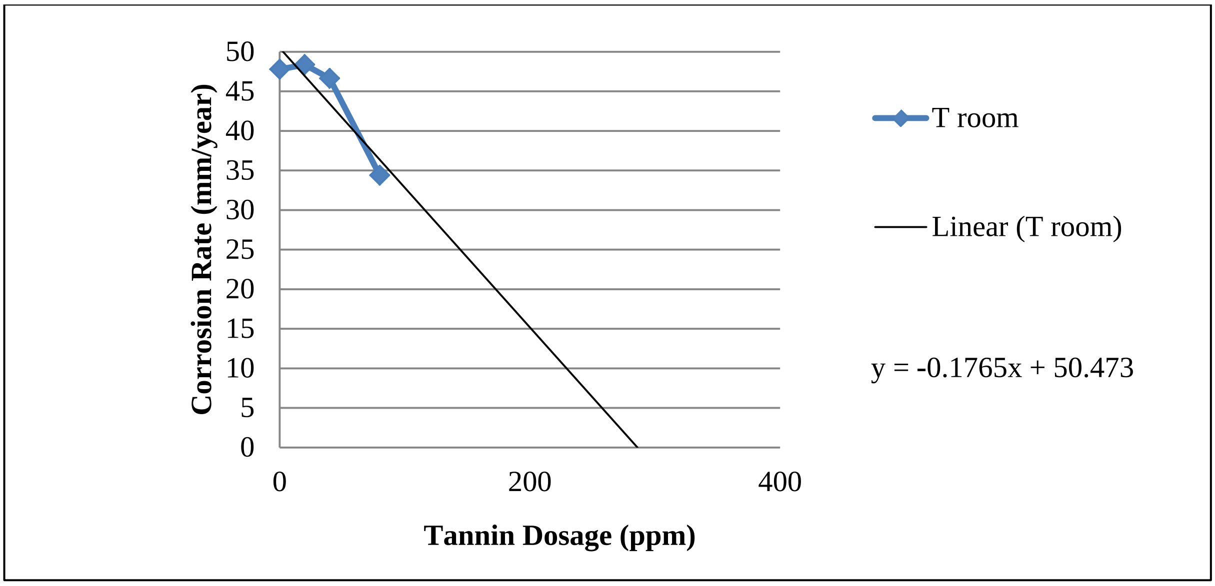

Figure 7. Linear Extrapolation of Carbon Steel Corrosion Rate to Tannin Dosage in 0.2 M Nitric Acid Solution

Corrosion Inhibition Mechanism

Some important parameters about the corrosion inhibition of carbon steel in nitric acid solution, that can be obtained from the cyclic voltammetry depicted in Figure 8, are:

1. The electron transfer occurs in single step reaction,
2. Carbon steel corrosion reaction is reversible,
3. The corrosion product, $Fe2^{+}$ ion was stable in the solution,
4. There is no indication of passivation.

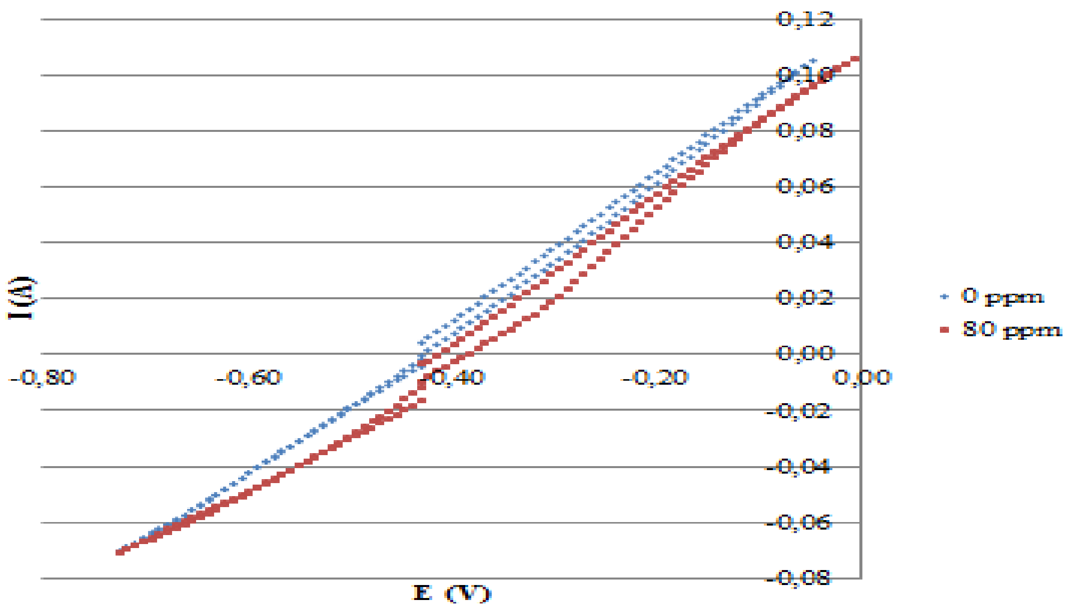

Figure 8. Cyclic Voltamogram of Carbon Steel in Nitric Acid Solution with Tannin Addition

Results of Fourier Transform Infrared (FTIR) Analysis

Figure 9 shows some peaks occuring at wave number of 3200-3500 cm^{-1} which represents the O-H bond (hidroxyl functional group bonding with hydrogen atom), and someother at 3500-3700 cm^{-1} which is characteristic of free O-H bond. The peak at 2500-3000 cm^{-1} shows the presence of carbocylic acid. The peak at 3300 cm-1 is a characteristic of aromatic compound, whereas the peak at 2850-3140 cm^{-1} (=C-H) and 1600-1680 cm^{-1} (C=C) shows the alkanes and alkenes functional groups. Ferric tannate was shown at 717.39-1376.93 cm^{-1}.

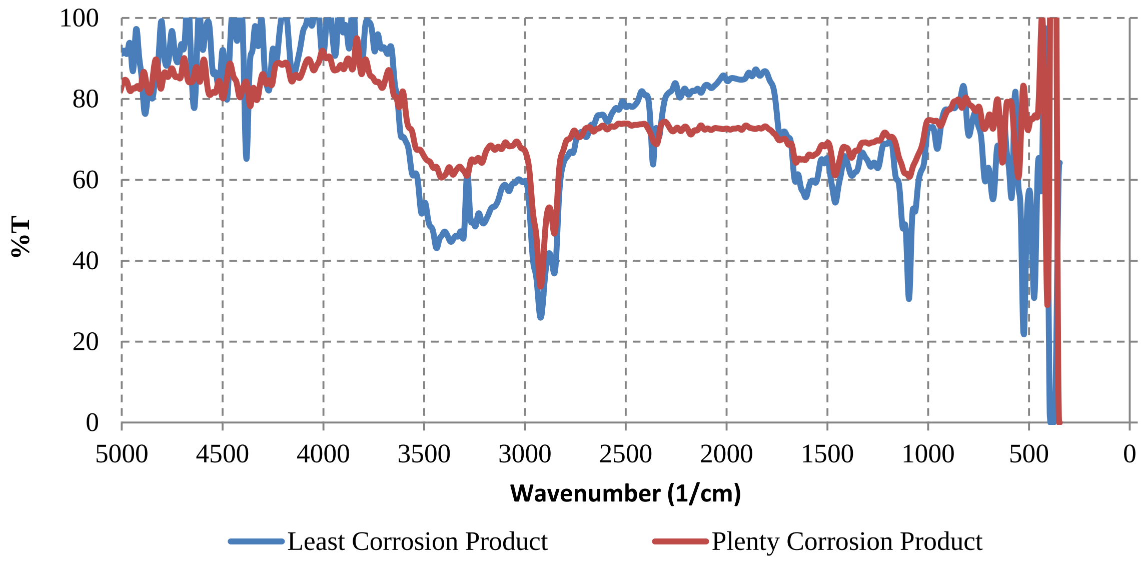

Figure 9. FTIR Spectra of The Corrosion Product

Based on the analysis of the samples, it can be seen that the peak at 1610 cm^{-1} shows that the C=C bond intensity was reduced, and at 3500-3700 cm^{-1} it shows that O-H bond intensity was also reduced. That indicates a possibility of adsorption at C=C and O-H bonds [4]. Hidroxyl functional groups at aromatic ring compound provoke tannin to form a ferric tannate complex in a sample which has the least corrosion product [11]. The test result also shows that sample which has plenty corrosion product did not indicate the presence of ferric tannate, it is really the opposite of the sample with the least corrosion product, which form a ferric tannate complex. This might be caused by the unability of oxide film to cover all of the steel surface, so there is still some part that can form a ferric tannate complex through the adsorption mechanism.

Different results were obtained in this experiment might be due to nitric acid as a strong oxidizing agent. Of the strong oxidizing characteristic induces the sterical effect to tannin, which make some or the entire tannin in the system cannot bind to carbon steel surface which is covered by oxide layer. Sterical effect can inhibit the complex formation due to the presence of large cluster attached to or adjacent with the donor atoms [2].

CONCLUSIONS

From the experimental results explained above, it can be concluded that:

1. Tannin is not an effective corrosion inhibitor for carbon steel in 0.1-0.4 M nitric acid solution at temperature range from room temperature to 60^{o}C.
2. The corrosion reaction of carbon steel in nitric acid solution with or without tannin addition is reversible, involving a single step oxidation-reduction reaction, resulting stable corrosion product, and not forming any passivation. The required tannin dosage to reduce carbon steel corrosion rate to less than 0.05 mm/year is more than 286 ppm.

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Nomenclatures

a	=	Relative atomic mass	[g/mole]
CR	=	Corrosion rate without inhibitor	[mm/year]
CRi	=	Corrosion rate with inhibitor	[mm/year]
Ep,a	=	Anodic peak potential	[mV]
Ep,c	=	Cathodic peak potential	[mV]
ΔEp	=	Distance between $E_{p,a}$and $E_{p,c}$	
F	=	Faraday constant	[C/moles of electrons]
i_{pa}/i_{pc}	=	Comparison of anodic and cathodic peak	[-]
K	=	Constant to equalize the Tafel's constant	[-]
n	=	Number of electron involved	[-]
r	=	Corrosion rate	[mm/year]
η	=	Inhibition efficiency	[%]

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