Corrosion control of carbon steel using inhibitor of banana peel extract in acid diluted solutions

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Abstract. Issues of corrosion happened in pipes, it was used as fluid transportation in the chemical industry. Corrosion cannot be preventing, however it could be controlled or blocked. Inhibitor addition is one of the method to control the corrosion inside the pipe. Corrosion inhibitors consisted of inorganic and organic compound inhibitors. Organic inhibitor is composed from synthetic and natural material. This study focused to evaluate the inhibition's efficiency from banana peel to carbon steel in different concentration of inhibitor and immersing time in acid solution variation. The research employed inhibitor concentration of 0 gram/liter, 2 gram/liter, 4 gram/liter and 6 gram/liter, immersed time of carbon steel for 2, 4, 6, 8 and 10 hours. It was immersed in chloride acid solution of 0.5 M and 1.5 M. Carbon Steel AISI 4041 was used as specimen steel. Results were analyzed using corrosion rate evaluation for each specimens and inhibitor efficiencies determination. It was found that the specimen without inhibitor yielded fast corrosion rate in long immersing time and high concentration of HCl. However, the specimens with inhibitor gave lowest corrosion rate which was 78.59% for 6 gram/litre and 10 hours in 0.5 M HCl.

1. Introduction

Metal is a fundamental raw material which supported in industry development thus it is very important role in human civilization. One of the uses of metal, as industry material is pipe production as fluid transportation tools. Generally, pipe channels are passed by various fluids types which caused the corrosion formed on the pipe wall.

Common metals which used for piping system are carbon steel because it considered more effective and economical. However, carbon steel has low resistance to corrosion. Metal utilization with better a corrosion resistance are a good option to choose. However, this method is rarely become the main choice for industries, since the increasing the durability of material means accompanied by increased cost. Therefore, protection methods is needed in order to decrease corrosion rate in carbon steel [1]. Method was used to protect internal carbon steel pipe are by adding corrosion inhibitor. Corrosion inhibitor is a chemical compound which added into the environmental, it able to decrease corrosion attack rate in metal. Inhibitors are divided into two types, organic and inorganic. Organic inhibitor is divided into synthetics and natural resources organic which also known as green inhibitor [2].

The aims of this research is to discover the inhibition effieciency in different concentration of banana peel's extract, determine the maximum banana peel's extract concentration as corrosion inhibitor of carbon steel in varied acid environment and immersing times and also to compare this study with the previos research regarding the banana's peel extract as corrosion inhibitor.
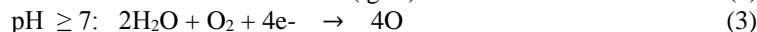
2. Literature review

Corrosion is degradation of metal due to redoks reaction between a metal to different substance in their environment then later produce undesirable compound [3]. Corrosion is also known as metal depletion rate or coronation. Corrosion is defined as attack that damages the metal since metal reacted with environment in chemically. Corrosion is a nature condition where every metal has its corrotion rate. Metal corrosion in eletctrolyte environment has impact from electrochemical process. Based on the electrochemical process, the necessity of the corrosion consisted of four main component [4], as listed below:

a. Cathode
    Generally, cathode does not undergo corrosion but it would be happen in certain conditions. Reactions in the cathode are reduction and it is depend to pH solution. As we can see the reaction below:

$$pH < 7 : \quad H^+ + e- \quad \rightarrow \quad H\ (\ atom\ ) \quad\quad\quad (1)$$
$$2H \quad\quad \rightarrow \quad H_2\ (\ gas\ ) \quad\quad\quad (2)$$
$$pH \geq 7: \quad 2H_2O + O_2 + 4e- \quad \rightarrow \quad 4O \quad\quad\quad (3)$$

b. Anode
    Commonly, anode have experience the corrosion by releasing electrons from its neutral metal atom in order to form the related ions. These ions still alive in the solution or reacted to form undissolved corrosion. Reaction for anode is listed as below.

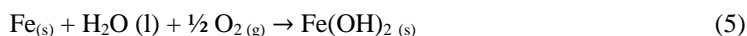$$M \quad \rightarrow \quad M^{Z+} + ze- \quad\quad\quad\quad\quad (4)$$

c. Anode and cathode should be electrically connected
    Between anode and cathode should be have the electrical connection so the current inside the corrosion cell able to flow. Physycal contact was unnecessary needed if anode and cathode has the same metal.
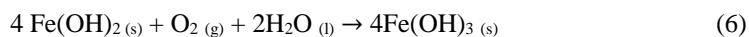
d. Electrolyte
    Electrolyte is a solution which has conductive properties. Electrolyte categorized to acid solution, base and saline solution. Electrolyte solution has important role in metal corrosion since this solution made electricity current between anode and cathode.

Corrosion process happen if half cell reaction which released electron (oxidation reaction in anodic side) and half cell reaction which received electron (reduction reaction in cathodic side). Both reaction will continue until reached the equilibrium dynamic where the released electrons amount equal to receive electrons. There are mechanism reaction of corrosion in iron (Fe) as shown [5]:

$$Fe_{(s)} + H_2O\ (l) + \tfrac{1}{2}\ O_{2\ (g)} \rightarrow Fe(OH)_{2\ (s)} \quad\quad\quad (5)$$

Ferro Hydroxide [$Fe(OH)_2$] is temporary result which oxidized naturally by water and air into Ferri Hydroxide [$Fe(OH)_3$] then the next reaction become:

$$4\ Fe(OH)_{2\ (s)} + O_{2\ (g)} + 2H_2O_{\ (l)} \rightarrow 4Fe(OH)_{3\ (s)} \quad\quad\quad (6)$$

Ferri Hydroxide formed changed into Fe_2O_3 which has brownish red called stain. Stain reaction can be shown :

$$2\ Fe(OH)_3 \quad \rightarrow \quad Fe_2O_3\ +\ 3H_2O \quad\quad\quad (7)$$

2.1 Corrosion rate

Corrosion rate has defined as amount of released metal for each time in certain surface. Generally, corrosion rate had noted in mils per year (mpy). Corrosion rate analysis has been held by using weight loss method as been seen [6]

$$CR = \frac{W \times 24 \times 365 \times 1000}{A \times T \times \rho} \qquad\qquad (8)$$

Equation 8 has elaborate in CR as corrosion rate (mm/y), W is mass of steel loss (gram) where $W = W_o - W_f$, W_o is initial weight (gram), W_f is final weight (gram), ρ adalah steel density (gram/cm^3), A is surface area of steel (mm^2), and T is immersing time (days).

2.1.1 Affected factors of corrosion rate
In metal, formation of corrosion has been influenced by several factors, They are: temperature, fluid flow, pH, and concentrations of corrosive material. They are describes:

a. Temperature
Temperature increase caused the accelerated the corrosion reaction rate. Since more elevated temperature made kinetic of the reacted more increased so exceeds the activated energy values. Therefore, it made the corrosion reaction rate faster and vice versa. However for open system, the ambient with above 80 ℃, the corrosion rate has been decreased since the oxygen would released while the closed system the corrosion rate will continue to increase due to oxygen dissolved content [7].

b. Fluid flow
Corrosion rate tend to increase if the fluid flow also getting raise. This is caused by contact between substance and metal get heighten so the metal ions will be loose which made metal experiencing fragility, its called corrosion [8]
c. pH
pH netral is 7, pH < 7 has properties like acidic and corrosive, pH > 7 with base and corrosive properties. However, for iron, low corrosion rate lies between 7 to 13 and it is increased below 7 and above 13 [4].
d. Concentration of corrosive material
Concentration of material corrosive related with pH or acidic and base of the solution. The acidic solution is highly corrosive to the metal where the metal in the acid solution medium will be more rapidly corroded because it is an anode reaction. Whereas, an alkaline solution can cause corrosion in the cathode reaction, since the cathode reaction always co-exists with the anode reaction and the reduction reaction always occurs simultaneously with the oxidation reaction known as the redox reaction.

2.1.2 Carbon steel
Generally, carbon steel is used for piping system because it is more effective and economic. Carbon steel was formed from main element of iron (Fe), second element was carbon compound which influenced to its properties while another element has influenced according to its percentages. Carbon steel contained three types, they are [9].
a. Low carbon steel
Low carbon steel has carbon content less than 0.3 and its micro structure devided into ferrit and perlite. Enhancement method used cold working method. This carbon has mild, firm and tough. Besides that, low carbon steel has good machinability and weldibility. It is commonly utilized because it is cheaper but it easy to corroded.

b. Medium carbon steel
Medium carbon steel has carbon content in range 0.3 – 0.6%. This steel can be enhanced its mechanic through heat of austenitizing, quenching, and tempering. It is widely used in tempering condition and has stronger properties than low carbon steels.

c. High carbon steel
High carbon steel has carbon content between 0.6-1.4%. This is the hardest, strongest, most brittle steel among the others and napless resistance. It is widely utilized in tempering condition so the

micro structure become martensite, and its mechanic properties is enhanced via heat of austenitizing, quenching, and tempering.

2.2 Corrosion control method

Metal protection technologies has been widely known to offer a better solution to solve corrosion problem. The utilized cost and method applications can be adjusted with condition and needs. There are several methods i.e. coating, cathodic protection, sacrificial anode method and inhibitor corrosion.

2.3 Types of corrosion inhibitor

Corrosion inhibitor was divided into inorganic and organic inhibitor. As describes as follows :

a.   Inorganic inhibitor

Inorganic inhibitor has active group, they are negative anion which useful to decrease corrosion rate to metal [10]. Generally, inorganic inhibitor are Sodium Nitrite, Chromat, Phosphat, and Zinc. The weakness of Sodium Nitrite is it is needed high concentration (300-500 mg/l) so it is not economical. Others, Chromat and Zinc are toxic and phosphate is considered as pollution compound since it improve phosphorous content in water [11]

b.   Organic inhibitor

Besides inorganic inhibitor, organic inhibitor has been developed. It is classified into synthethic organics and organic from nature's extraction [2]. Compounds used as organic inhibitors are compounds with consisted of nitrogen, sulfur or oxygen atoms having a pair of free electrons. According to Stupnisek-Lisac et al, [12], the more effective inhibitor for metal corrosion is organic compounds. This is caused the organic compound has free pair of electrons in their carbon chain or in the aromatic chain systems which able to bind to metal positive charge so the adsorption between metal surface and inhibitor happened. This adsorption formed protector layer in the metal surface due to physysorption or to generate chelate barrier that does not dissolve as a result of chemisorption process. It could inhibite metal from direct contact with corrosive media [13].

 Organic inhibitor of natural material come from natural matter extraction which contained nitrogen, oxygen, phosphor and atomics with free electron pairs. Elements which has free electron pairs has function as ligan to generate complex compound with metal and will cover its metal from corrosion attacks. This is called as "green inhibitor" since it is benign to environment, inexpensive, easy to get and applicable to environment. Todays, a lot of researchers has been developed the green corrosion inhibitors [14].

Several plant has been investigated its ability as organic inhibitor corrosion such us mangoness peel, tea leaves, and acacia barks. Researches about mangoness peel extract as inhibitor for 200 ppm in H_2SO_4 0.02 M for 24 h generated inhibition efficiency around 48.79% [15]. Tea leaves *Camellia sinensis* produced 86.3% efficiency in HCl 3% medium for 4 days [16]. Accacia's bark generated 36.1% in 80 ppm to feed water boiler in 65°C[2]. Eddy and Ebenso [17] investigated banana's peel (*Musa Sapientum*) in H_2SO_4 2.5 M as corrosion inhibitor. Their research had obtained efficiency around 71.05% in 0.5 g/l in 303 °K for immersing temperature.

2.4 Tannin compound

Another natural were used as organic inhibitor corrosion is tannin. It is a polyphenol compound, and it is also able to form complex coumpund and indissolved to metal ions. Complex compound generated between tannin and metal ions will cover the metal from direct contact of corrosive fluid so the corrosion rate of metal has been decreased [2]. Figure 2.1 illustrates the tannin core molecule structure.
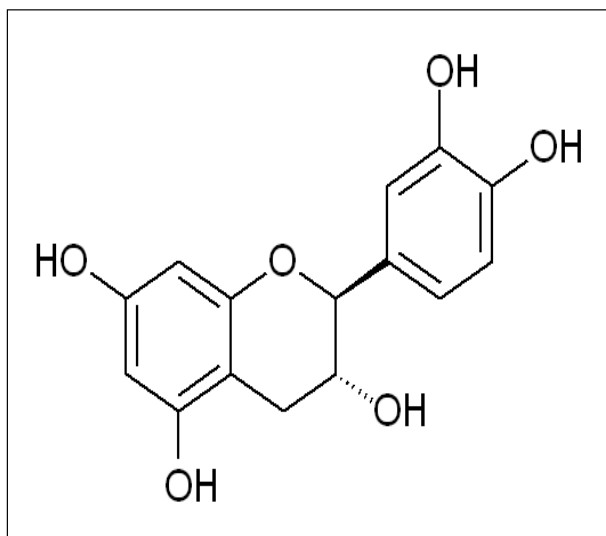.

Figure 1. Sturcture of tannin molecule.

Tannin is a massive phenol compound with large molecule weight. Tannin is macromolecule compound with polar polyphenol group thus tannin extraction product is able to conduct by using polar solvent [18]. Tannin is found in almost every green flora with different content and qualitative [19]. Tannin can inhibit the corrosion since it generated a mixture complex compound of iron and tannin. This compound cover the surface of metal and useful to detain corrosion. Iron is metal transition, its properties in transition side is to tend produce complex ions or compounds. Ions from iron has empty orbital which able to receive electrin couple from tannin into d^2sp^3.

a. Qualitative analysis of tannin
Tannin qualitative analysis is an analysis to identify the presence of tannin plant extracts. The method is $FeCl_3$ of 1%. The presence of tannin is detected with the change color into greenish black if it is reacted with $FeCl_3$ since tannin in the extrac engender complex compound with ion Fe^{3+} [20].

b. Analysis quantitavie of tannin
Qualitative analysis is conducted to analyze the percentage of tannin in the extract's product. It is determined by using *Folin Ciocalteau* method. This method was using reagen *Folin Ciocalteau* since phenolic compound able to react with folin to form blue coloreed solution which measured the absorbance using spectrofotometre. Phenolic compound only reacted with *Folin Ciocalteau* in base ambient so the proton dissosiasion in phenolic compound into phenolic ion.. Therefore, it employed Na_2CO_3 15% for base condition in solution [21].
Next, the solution is measured by using UV-Vis Spectrofotometre. The absorb spectrum was shown in the outside electron energy change from a molecule which caused the emerging of bond or not chemical bond. Generally, energy change happen caused by the carbon double bond or nitrogen pairs with oxygen. Tannin compound contain conjungated aromatic system, therefore it depicted the strong absorption bands in ultraviolet and visible range [20].
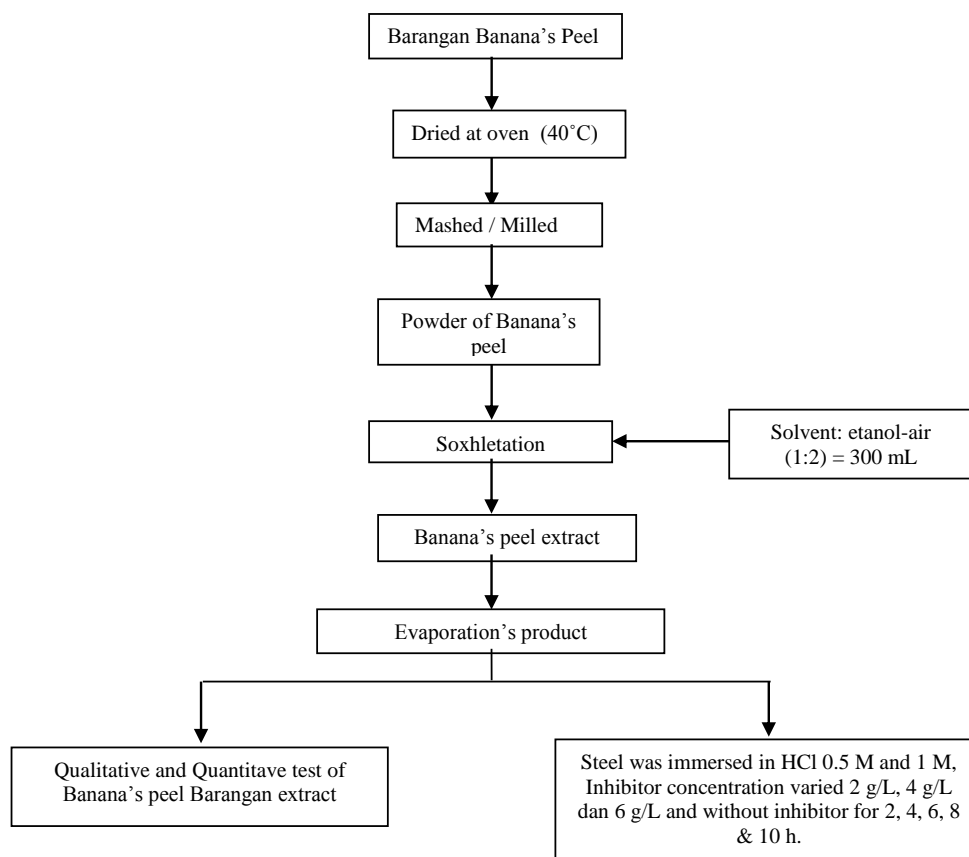
3. Methods

Figure 2. Diagram of banana peel extraction and corrosion rate analysis.

4. Results and discussion

Crude tannin extraction from banana's peel was held by soxhletaion method. It was evaporated to eliminate the solvent then condense the extract's product. In soxhletation process, ethanol: water ratio was 1: 2 for ± 8 h was conducted. Tannin is a polar compound, therefore etanol-water as polar compound is able to extract it. As in solvent side, ethanol-water mixture was used to obtain the amounts of extracted material [23]. The products extraction waere evaporated to omit the remaining solvent and to concentrate extract's product. Qualitative analysys or phitochemical test was held to assest the presence of tannin in extracts banana's peels. Phitochemical test was conducted by adding $FeCl_3$ reagen into guava leaves extract which showed the greenish or blue ink color change.

   Phythochemical test has been done using $FeCl_3$, it is to determine either sample contained phenol group or not. After its change then the sample might contain phenol compound and it would might be proven the presence of tannin. This color changed occurred since the reaction between tannin and $FeCl_3$ produced the complex compound which made the mixture became greenish black color. Quantitave analysys of crude tannin was determined by using phenolic analysis method (Folin-CioCalteu) since tannin is one of phenolic compound which contained in plants. This method using regression linear equation as $y = 0,005x + 0,021$ from the calibration curve, y is absorbance value from Atomic Absorption Spectroscopy (AAS) analysis and x is crude tannin concentration in banana's peel (ppm). In soxhletation process, it was found that the absorbance was 0.1061 by twenty times dilution process then it was estimated that the crude tannin concentration in banana's peel sample was 340.4 ppm.
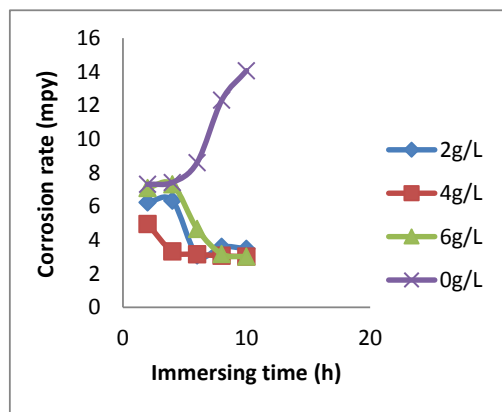
Figure 3. Immersing time vs corrosion rate in HCl 0.5 M.
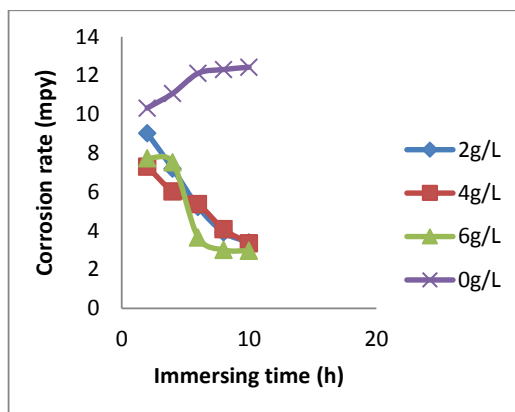

Figure 4. Immersing time vs corrosion rate in HCl 1 M.

   Base on Figure 3, it shown that the lower corrosion rates were obtained by adding the inhibitor, it was contrary to the sample without inhibitor addition. It was occured because the presence of tannin in the banana's peel extract. Tannin is a complex poliphenol compound, where tannin molecule adsorpsed in the metal surface and formed a thin layer. This layer is unable to see by directed eyes, but it can detained the corrosion process in metal.   Figure 4 depicted the difference of corrosion rate inside the HCl 0.5 M solution by adding and without the inhibitor. The lowest corrosion rate was reached at amount 3.0118 mpy in 6 g/l inhibitor concentration for 10 h while the highest corrosion rate reached out in 7.3143 mpy for 4 h in 6 g/l inhibitor concentration. It was proved that tannin has potential to decrease the corrosion rate thus it able to to use as inhibitor for shelving the corrosion rate.

   Immersing time did influenced the corrosion rate. Figure 3 and 4 shown that the longer immersing time made the corrosion rate became more decelerate. It showed that more consuming contact time between tannin molecules with metal surface which formed thin layer protection then the corrosion rate was decreased and corrosion product $Fe(OH)_3$ able to cover the metal surface to develop pasive layer in cathode side then it affect reduction reaction in cathode. If reaction in cathode was inhibited, steel oxidation in anode would be inhibited.

   In Figure 4 there is the difference of corrosion rate steel in HCl 1 M by adding and without inhibitor. The lowest corrosion rate was 2.9688 mpy in 6 g/l inhibitor concentration for 10 h while the highest corrosion rate was achieved 7.5294 mpy for 4 h and 6 g/l concentration inhibitor.
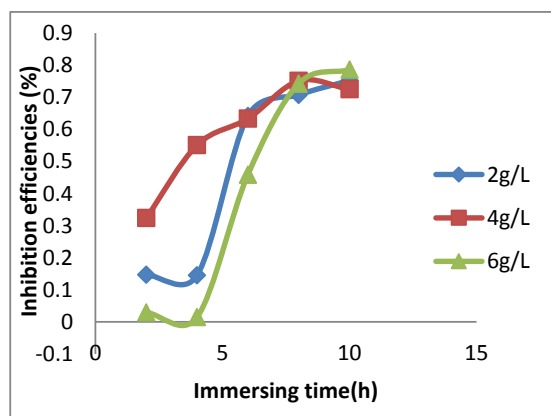

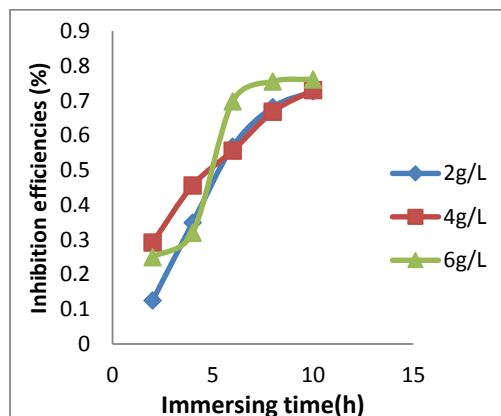**Figure 5**. Immersing time vs inhibitor efficiencies in HCl 0.5 M.

Figure 6. Immersing time vs inhibitor efficiencies in HCl 1 M.

Figure 5 shown the highest efficiency of inhibition 78.593% for 10 h in 6 g/l inhibition addition. It was proven in the theory, the inhibition concentration depended on immersing time. When the contact time take more prolonged between metal and corosive media made larger inhibition efficiencies, and also the oppposite ways. Figure 6 shown the highest efficiency inhibition at 76.125% in 6 g/l inhibitor addition for 10 h.

This results showed that the presence of tannin in the banana's peel has not fully formed complete complex compound then it was uncovered the entire surface of steel metal.

5. Conclusion

Banana's peel extract was proven as corrosion inhibitor because of the presence of tannin in the banana's peel. Lowest corrosion rate was obtained at 3.0118 mpy in 0.5 M HCl and 2.9688 mpy in 1 M HCl for 10 h and 6 g/l inhibitor concentration. Immersing time influenced the corrosion rate. The lower corrosion rate occured for longest immersing time. Highest inhibition obtained 78.593% and 76.125% for 10 h and 6 g/l inhibitor concentration in 0.5 M and 1 M HCl, respectively.

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