Protection of mild steel from corrosion using methanol extract of avocado (*Persea americana mill*) seeds in a solution of sulfuric acid

D R Gusti¹, I Lestari, F Farid, P T Sirait

Chemistry Department, Faculty of Science and Technology, Jambi University, Jambi, Indonesia

Email: ¹diahgusti07@yahoo.co.id

Abstract. Avocado seeds have been studied for use as corrosion inhibitors of mild steel in a solution of 0.75 M sulfuric acid. Corrosion inhibition efficiency at a concentration of 10 g / L avocado seed extract (ASE) was obtained at 74.56% with weight loss method and 68.38% with potentiometric polarization method. Corrosion inhibition efficiency was found to be greater with increasing ASE concentration. Polarization studies show that the avocado seed extract is a mixed corrosion inhibitor. SEM images on mild steel with the addition of ASE showed the formation of a thin layer on the mild steel surface. OH and CN functional groups appear on the FT-IR spectrum of ASE. These functional groups interact with iron on the steel surface to form a thin layer that can inhibit corrosive ion attacks from sulfuric acid solutions.

1. Introduction

Mild steel is the most extensively used metal for construction and industrial applications because it is easily obtained, fabricated, and high tensile strength. However, the shortage of steel is highly susceptible to corrosion in the corrosive medium which has an impact on economic and environmental losses [1-3]. The most industries used acid solution for preservation, cleaning, and maintenance processes. The acid solution is among the factors that drive corrosion problems. Corrosion causes a reduction in the mechanical properties of steel such as strength, tenacity, reduction of thickness, and degradation of the material [4, 5].

Corrosion prevention can be carried out such as by coating on metal surfaces, cathodic protection, and adding corrosion inhibitors. The use of corrosion inhibitors has been widely reported and is very efficient to control the corrosion process [6]. Corrosion inhibitors can be inorganic, organic, or mixed compounds. Inorganic inhibitor compounds used include sodium chromate, phosphate, and molybdate which have toxic and carcinogenic properties. Generally, organic compounds that are effectively used as corrosion inhibitors are compounds that have electronegative functional groups such as S, O, P or N and double bonds in molecules. It can be adsorbed on the metal surface [7, 8]. An important criterion for applying an inhibitor to a large-scale industry is that it can be broken down by microorganisms, not toxic, and not the pollutant so that it is safe for the environment and health [6, 9].

Today, researchers are developing more natural corrosion inhibitors that are environmentally friendly, non-toxic and easily obtainable. Plant extracts are very rich with natural chemical sources. It can be extracted to use simple procedures, inexpensive and easily decomposed in nature [10]. Several studies using natural extracts such as cocoa seed extract (*Theobroma cacao*) containing tannins,
phenolics, alkaloids, and flavonoids could inhibit steel corrosion in NaCl by 91.93% [11]. Corrosion inhibition efficiency of Coromandelica leaf extract containing flavonoids, tannins, terpenoids, and polysaccharides against steel in sulfuric acid solution was 93.8% [12]. Peumus boldus leaf extract containing phenolic and alkaloids has been reported as a corrosion inhibitor in sulfuric acid solution with an inhibition efficiency of 73% [13].

Tannins and flavonoids are also found in avocado seeds. Avocado seeds are waste that has not been used optimally. Therefore, it is necessary to transform avocado seeds which were originally waste into a product that has a high value. Avocado seeds besides containing phenolic and flavonoids also contain triterpenoids, quinones, saponins, tannins, monoterpenoids and sesquiterpenoids, even tannin content of 13.6% tannins and 13.25% starch [14]. Based on the chemical compounds contained in the avocado seeds it is thought to have the potential as a corrosion inhibitor biomaterial. Therefore, research is needed on the ability of avocado seed extract to inhibit corrosion in steel so that it can be used as a corrosion inhibitor.

2. Experimental procedures

2.1. Solutions and samples preparation
Mild Steel composition as follow 98.5% Fe, 0.19% C, 0.22% Si and 0.654% Mn. Rod-shaped steel cut in size 2 x 1 x 0.1 cm. Specimens were ground the surface by using iron sandpaper and then cleaned using aquadest and acetone to remove fat that might stick to the specimen. Then dried using an oven at 50°C. After drying, the steel is measured in length and width and weighed in mass. The result of weighing is expressed as the initial mass (m1).

Avocado seed dry powder 500 g was extracted with methanol in maceration for three days. The macerated extract is filtered. The filtrate was collected while the residue was re-extracted with ethanol for three days then filtered again. The filtrate is concentrated using a rotary evaporator so that the concentrated extract is obtained. The concentrated extract was air-dried to remove the solvent.

The corrosive solution is 0.75 M H2SO4 solution. Avocado seed extract solution with a concentration of 10 g/L as a stock solution with 0.75 M H2SO4 solvent. From this stock solutions, the inhibitor solutions were prepared with the different concentration of 2, 4, 6, 8 and 10 g / L respectively as test solutions.

2.2. Weight loss measurement
Mild steel is soaked in sulfuric acid with and without avocado seed extract at various concentrations for 72 hours. After soaking is finished, the mild steel is cleaned with a soft brush, washed them using distilled water, rinse with acetone, and then dried in the oven at 50°C. After drying the steel is weighed and the weighing results are expressed as final weight.

2.3. Measurement of Potentiodynamic Polarization
Measurement of potentiodynamic polarization, mild steel was used as a working electrode with a size of 2 x 1 cm, Pt electrode as a support electrode and Ag / AgCl as a comparative electrode. Potentiodynamic polarization measurements are carried out using eDAQ potentiostat. It was carried out in 0.75 M sulfuric acid solution without and with presence of a mixture of concentrations of inhibitor concentrations 2.0 g / L; 4.0 g / L; 6.0 g / L; 8.0 g / L and 10 g / L respectively. Three electrodes are dipped in a vessel containing corrosive media without and with the addition of an inhibitor. Then connect to the potentiostat and measure the potential so that the relationship curve between potential (E) and current (I) is obtained.

2.4. Fourier Transform Infra-Red (FTIR) Analysis
FTIR measurements were carried out by taking corrosion products (rust) attached to steel, then the corrosion product was washed, dried and analysed with FTIR using KBr pellet plate, FTIR measurements were also made for avocado seed extract.

2.5. Scanning Electron Microscopy (SEM) Analysis
The steel was dried after soaking for 72 hours in sulfuric acid without and in the presence of avocado seed extract, then performed Scanning Electron Microscopy (SEM) analysis with 1000 times magnification.

3. Result and Discussion

3.1. Weight loss measurement
Corrosion rate in H\textsubscript{2}SO\textsubscript{4} solution with avocado seed extract has been studied by weight loss method using the following equation [15]:

\[ C_R = \frac{W_b - W_a}{S \cdot t} \]  

Where \( C_R \) are corrosion rate, \( W_b \) dan \( W_a \) are the sample weight measured before and after soaking in a solution of corrosive. \( S \) is exposed area and \( t \) is time in hour.

Inhibitor Efficiency (IE \%) is calculated by following equation [15, 7]:

\[ IE(\%) = \frac{C_R(\text{blank}) - C_R(\text{Inh})}{C_R(\text{blank})} \times 100\% \]  

3.1.1. Corrosion rate of mild steel in sulfuric acid solutions. Figure 1 showed, corrosion rates of mild steel in sulfuric acid solutions are higher with increasing concentrations of sulfuric acid. This is because more H\textsuperscript{+} ions produce H\textsubscript{2}. H\textsuperscript{+} ions are very aggressive in attacking steel, oxidizing Fe to Fe\textsuperscript{2+} which causes corrosion. The stages of the corrosion process that occur based on equation (1) are as follows [15]:

\[ \text{Fe (s) + H}_2\text{O (l) + }\frac{1}{2}\text{O}_2 (g) \rightarrow \text{Fe}^{2+} (aq) + 2\text{OH}^- \]  

The formed Fe\textsuperscript{2+} ion can be oxidized again to form Fe\textsuperscript{3+} ions due to the presence of excess oxygen in the solutions of sulfuric acid. The Fe\textsuperscript{3+} ions react back with oxygen and the water molecules form rust as in equation (2), which is as follows [15]:

\[ 2\text{Fe (OH)}_2 (s) + \text{H}_2\text{O (l) + }\frac{1}{2}\text{O}_2 (g) \rightarrow 2\text{Fe (OH)}_3 (s) \]  

![Figure 1. Correlation between different concentration of H\textsubscript{2}SO\textsubscript{4} dan corrosion rate.](image)

3.1.2. Analysis of the effect of sulfuric acid concentration with the addition of avocado seed extract to the corrosion rate and corrosion inhibition on mild steel. Figures 2 and 3 show the effect of adding avocado seed extract to the corrosion rate and the efficiency of corrosion inhibition. Corrosion rates without the addition of ASE have a greater corrosion rate than the addition of ASE. As the
concentration of ASE increases, the corrosion rate decreases, and the efficiency of corrosion inhibition increases. This indicated that ASE is adsorbed on the mild steel surface so that it covers the surface and inhibits the corrosive ion attack on the mild steel surface. Thus, the corrosion rate decreases, and the efficiency of corrosion inhibition increases. Corrosion inhibition efficiency on mild steel with an avocado seed extract inhibitor concentration of 10 g / L for 72 hours is 74.55%.

Figure 2. Avocado seed extract concentration variation on corrosion rate of mild steel for 72 hours.

Figure 3. The effect of the inhibitor concentration of avocado seed extract on the corrosion inhibition efficiency on mild steel.

3.2. Polarisation potensiodynamics method
Potentiodynamic polarization curves are extrapolated using the Tafel method. Potentiodynamic polarization curves with and without of avocado seed extract are shown in Table 1. Measurement of potentiodynamic polarization with Tafel plot of polarization curves can be used for corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$) inhibition efficiency (% EI), cathode tafel constant (βc) and anode tafel constant (βa). The value of the polarization curve is shown in table 1.
Table 1. Corrosion parameters obtained potentiodynamic method for corrosion of mild steel in 0.75 M sulfuric acid with different Avocado Sees Extract (ASE) concentration

| ASE Concentration (g/L) | E_corr (v) | I_corr (mA/cm²) | β_a (V) | β_c (V) | EI (%) |
|-------------------------|------------|-----------------|--------|--------|-------|
| Blanko                  | 0.630      | 7.58 x 10⁻⁵     | 0.055  | 0.075  |       |
| 2                       | 0.150      | 7.41 x 10⁻⁵     | 0.046  | 0.057  | 2.27  |
| 4                       | 0.170      | 6.02 x 10⁻⁵     | 0.050  | 0.070  | 20.56 |
| 6                       | 0.635      | 3.39 x 10⁻⁵     | 0.043  | 0.050  | 55.33 |
| 8                       | 0.625      | 3.02 x 10⁻⁵     | 0.064  | 0.060  | 60.18 |
| 10                      | 0.640      | 0.000024        | 0.040  | 0.058  | 68.37 |

Table 1 shows that the current density is higher in the absence of avocado seed extract. The addition of the concentration of avocado seed extract reduces the current density and increases the efficiency of inhibition. This is due to the formation of layers on the steel surface by avocado seed extract which inhibits the occurrence of corrosion processes [16,17].

The inhibitory efficiency of steel corrosion by avocado seed extract inhibitors at a concentration of 10 g / L was 68.37%. The value of the inhibition efficiency obtained from the potentiodynamic polarization is different from the calculated value using the weight loss method. This is due to the time difference required by the inhibitor to be adsorbed and form a mild steel surface layer [16].

Anodic Tafel constants (β_a) and cathodic Tafel constants (β_c) show the potential for small changes after addition of avocado seed extract. Small changes in β_a and β_c indicate that the mechanism of corrosion does not change with the addition of inhibitors [19]. The inhibitor molecule is adsorbed on the soft steel surface by blocking the active site for the reaction [17].

Table 1 shows the displacement of the cathode and anode curves. If E_corr value showed a more negative shift from blank solution, it is called a cathodic inhibitor where inhibitors inhibit the evolutionary reaction of hydrogen. E_corr value experienced a shift to a more positive direction than the blank solution called an anodic inhibitor where the inhibitor inhibited dissolution of the iron anode [20]. E_corr value experiences a positive and negative shift from blank solution is called a mixed inhibitor [4]). E_corr value of avocado seed extract has a positive shift from blank or anode solution at a concentration of 2 g / L, 4 g / L, and 8 g / L. It indicated the inhibition of iron dissolution at the anode occurs. A shift towards negative or to cathodic at concentrations of 6 and 10 g / L explains the inhibition of hydrogen evolution. Based on these data, avocado seed extracts are classified as mixed inhibitors [17].

3.3. Fourier Transform Infra Red (FTIR) Analysis

Fourier Transform Infra Red (FTIR) analysis is used to identify functional groups that act as corrosion inhibitors of secondary metabolites contained in avocado seed extract. Each compound has its own specific functional group (Fig 5). Compounds that can be used as corrosion inhibitors are compounds that have hydroxyl (OH-), carboxyl (―COOH) functional groups, carbonyl (―CO), ―CO―, CH, ―C = C―, ―C≡C―, - C - Cl, amines (―C≡N) and others that have electron pairs that can interact with Fe on the metal surface. The infrared spectrum is used to determine functional groups that act as corrosion inhibitors of secondary metabolites contained in avocado seed extract.
The FTIR spectrum of ASE in Figure 4 (a) shows the absorption band of the -O-H group at a wave number of 3339.13 cm\(^{-1}\) with a wide peak. The C≡N group absorption band at wave number 2168.22 cm\(^{-1}\) with a sharp absorption peak and weak intensity. The presence of C = O is at wave number 1719.22 cm\(^{-1}\) with a weak absorption peak. Aromatic C = C functional group at wave number 1522.29 cm\(^{-1}\). C = C (alkene) is at wave number 1616.51 cm\(^{-1}\) with a sharp absorption peak and the presence of CN at wave number 1166 cm\(^{-1}\) with a sharp absorption peak and strong intensity. From the infrared spectrum, avocado seed extract contains a chemical functional group that acts as an environmentally friendly corrosion inhibitor.

Figure 4 (b) shows a shift in wave numbers indicating the interaction between functional groups and metal surfaces. The -OH group with wave numbers 3339.13 cm\(^{-1}\) shifts to 3158.86 cm\(^{-1}\) and the resulting peak is wider. The C≡N group with wave numbers 2168.22 cm\(^{-1}\) shifts to 2344.03 cm\(^{-1}\) with
sharp absorption peaks and weak intensity, group C = C shifts from wave number 1616.51 cm\(^{-1}\) to 1631.71 cm\(^{-1}\) with a sharp absorption peak.

Figures 5 (a) and 5(b) show different spectrum patterns. Changes in the wave number shown by the infrared spectrum indicate an interaction between the compounds contained in avocado seed extract and steel through the extraction of extracts on the steel surface.

3.4. Morphology of mild steel surface
Steel surface morphology is not soaked and soaked in 0.75 M H\(_2\)SO\(_4\) in the absence and presence of 10 gL\(^{-1}\) ASE for 3 days at room temperature, were examined by SEM. SEM micrograph in Fig.1b explained that the mild steel surface shows a very porous and rough surface in the absence of ASE in 0.75 M H\(_2\)SO\(_4\) solution due to corrosive attack by acid solution. In the presence of ASE (Fig.1c), SEM micrograph exhibited unporous and smooth surface. It shows to inhibition effect of ASE. This is because the steel surface has been covered by avocado seed extract which forms a thin layer. This thin layer formation is caused by the interaction between functional groups of compounds contained in avocado seed extract with soft steel, so that the steel surface is protected and protected and can inhibit corrosion rate [21].

![SEM image](image1.png)

**Figure 5.** SEM image for mild steel surface before treatment (a), mild steel after immersion in 0.75 H\(_2\)SO\(_4\) in the absence of ASE for 3 days at room temperature (b), mild steel after immersion 0.75 M H\(_2\)SO\(_4\) in the presence of 10 gL\(^{-1}\) ASE for 3 days at room temperature (c).

4. Conclusion
Corrosion inhibition efficiency increases, and corrosion rate decreases on mild steel with increasing concentration of avocado seed extract. Corrosion inhibition efficiency in ASE 10 g / L in 0.75 M H\(_2\)SO\(_4\) solution for 72 hours on mild steel is 74.55%. ASE can be classified as a mixed inhibitor because it can inhibit corrosion reactions at the anode and cathode. FTIR spectroscopic analysis and SEM showed the coating on steel surfaces which inhibited corrosion. ASE is a good corrosion inhibitor.

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