Exploration of coffee bean husks waste as an eco-environmentally friendly corrosion inhibitor on mild steel in sulphuric acid solutions

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Abstract. Coffee bean husks waste contains chemical compounds such as tannins and flavonoids. These compounds are known to inhibit corrosion. Corrosion inhibition of mild steel in 0.75 M \( \text{H}_2\text{SO}_4 \) has been investigated using the presence and absence of coffee bean husk extract (CBHE). The effect of inhibition efficiency and corrosion rate on extract concentration and immersion duration was studied using the method of weight loss. The inhibition efficiency increases and the corrosion rate decreases with increasing immersion time and the concentration of CBHE. The corrosion inhibition efficiency was obtained 97.54 % obtained at 72 hours immersion and addition of CBHE 10 g/L. Steel surface adsorption was examined by SEM and FTIR spectroscopy. CBHE is recommended as a good inhibitor.

Keywords: coffee bean husk; corrosion inhibitor; mild steel; steel surface adsorption

1. Introduction
Coffee is a popular food industry product in the world and is the most important product after crude oil. In the processing of coffee produced as much as 40-45 % of coffee bean husks waste. Esquivel and Jimenez et al. (2012) reported that coffee skin waste is pulp (mesocarp section), skin (exocarp section), mucilage and parchment (endocarp section). Coffee bean husks are one part of coffee bean waste produced in the coffee bean processing. In general, coffee husks waste is only used as animal feed. The lack of public awareness and the lack of information about the benefits of using coffee husk waste causes the absence of utilization and processing of the coffee husk waste. The composition of the coffee skin and pulp has similarities with the husk. There are four main classes of polyphenols found in Arabica coffee pulp viz flavan-3-ols, hydroxycinnamic acids, flavonols, and anthocyanidins. [1]. Phenolic compounds contain OH functional groups can interact with Fe on steel [2].

Recent research developments, corrosion inhibitors of plant extracts have been widely studied such as avocado seed extract [2], cassava leaf extract [3], saracha ashoka extract [4], strumarium extract Xanthium[5], etc. containing polyphenolic compounds. Inhibitors of plant extracts are more environmentally friendly than inorganic inhibitors. Corrosion inhibitors are indispensable for steel protection. Steel is easily corroded in acidic solutions. Steel is widely used in industrial processes, so damage to steel results in huge losses for the industry.

Inhibitor of coffee bean husks extract is one alternative to organic corrosion inhibitors of environmentally friendly, inexpensive and easily obtained. In this study, the inhibitory properties of coffee bean husks extract were studied through weight loss and potentiodynamic polarization methods.
Characterization of steel surface layers was tested on Fourier Transform Infra-Red (FT-IR) and Scanning Electron Microscopy (SEM).

2. Experimental Procedure

2.1. Sample preparation
Mild steel (98.5 % Fe, 0.19 % C, 0.22 % Si, and 0.654 % Mn) are cut at 2 × 1 cm in size. The sample is brushed with emery paper, then washed with distilled water and dried with a cleaning tissue, dipped in acetone and then dried again, next the steel is weighed. The weight of the steel is called the initial weight \(m_1\).

The powder of coffee bean husks (500 g) was macerated using methanol solvent for 3 days. The maceration extract was filtered using a buchner funnel and the filtrate was concentrated using a vacuum rotary evaporator. Coffee bean husk extract (CBHE) was prepared 2, 4, 6, 8, and 10 g in 1L \(H_2SO_4\) with a concentration of 0.75 M. Mild steel is dipped in a solution of sulphuric acid without and the presence of CBHE for 24, 48, and 72 hours, then mild steel is cleaned with water and washed with acetone, and then dried with cleaning tissue and weighed. The steel is weighed and the steel weight after treatment \(m_2\).

2.2. Potentiodynamic polarization measurement
Polarization potentiodynamic used by the EDAQ Potentiostat Electrochemical System which consists of 3 electrodes, Pt electrodes as supporting electrodes, Ag / AgCl electrodes as reference electrode and working electrode in the form of steel samples used in this study. Three electrodes were immersed in 0.75 M sulphuric acid solution without and with CBHE at concentrations of 2, 4, 6, 8 and 10 g/L and obtained a graph, in the form of potential \(E\) with current \(I\).

2.3. Fourier transform infra-red (FTIR) spectroscopy analysis
Mild steel samples were immersed for 3 days in a mixture of inhibitors and 0.75 M HCl. The mild steel sample was dried then scraped off and produced powder. The inhibitors and powder samples were each mixed with KBr and transferred to pellets for subsequent analysis using the FT-IR spectrum.

2.4. Scanning electron microscopy (SEM) analysis
Steel after immersion in sulphuric acid for 72 hours in the presence or without CBHE was analysed by surface morphology with Scanning Electron Microscopy (SEM) with magnification 1000 times.

3. Results and Discussions

3.1. Weight loss method
Weight loss method is used to study the effect of adding CBHE to the rate of corrosion of mild steel and the value of inhibition efficiency in sulphuric acid corrosion medium. Weight loss method is based on weight loss before and after the corrosion process. The mild steel was immersed in a solution of sulphuric acid with 0.75 M and the steel immersion was varied for 24, 48 and 72 hours in the presence of CBHE 2, 4, 6, 8, and 10 g/L. The mild steel corrosion rate is calculated using equation (1) [6][7].

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

where “CR are corrosion rate, \(W_b\) dan \(W_a\) are the sample weight measured before and after soaking in a solution of corrosive. S is surface area and \(t\) is time in hour”.

The efficiency of mild steel corrosion inhibition is calculated using equation 2 [2][8]:

\[
IE (\%) = \frac{CR (blank) - CR (inh)}{CR (blank)} \times 100 \%
\]
where “CR (blank) and CR(Inh)” indicate corrosion rate the absence and presence of CBHE in the sulphuric acid solution”.

Figures 1 and Figure 2 illustrate the measurement of weight loss methods with varying concentrations of CBHE successively 0, 2, 4, 6, 8, and 10 g/L, against the variation of immersion time used respectively 24, 48 and 72 hours. Corrosion rate decreases and corrosion inhibition efficiency increases with the presence of CBHE compared to without the presence of CBHE. The effect of CBHE on the corrosion rate is shown in Figure 1 and inhibitory efficiency in Figure 2.

The corrosion rate is reduced and inhibition efficiency increases with increasing concentration. It is caused by coating on the steel surface which prevents corrosion attacks and slows the occurrence of corrosion reactions [9,10]. The surface layer is formed by CBHE which is absorbed on the mild steel surface. The highest inhibitory efficiency was 97.543 % with the addition of 10 g/L CBHE during the 72 hour immersion time.

![Figure 1](image1.png)

**Figure 1.** Correlation between CBHE concentration and corrosion rate for three days immersion in 0.75 M sulphuric acid solution

![Figure 2](image2.png)

**Figure 2.** Correlation between CBHE concentration and inhibition efficiency for three days immersion in 0.75 M sulfuric acid solution
3.2. Polarisation Potensiodynamic Method

Potentiodynamic polarization methods can provide information about the dissolution of iron at the anode and the reduction of hydrogen ions at the cathode [11]. Mild steel measurements in the potentiodynamic polarization method with varying CBHE concentrations produce a potentiodynamic polarization curve for mild steel in 0.75 M H₂SO₄ containing various concentrations of CBHE which is shown in Table 1.

**Table 1.** Potentiodynamic polarization data from mild steel without and presence of CBHE in 0.75 M sulfuric acid solution

| Concentration g/L | Ecorr (V) | Icorr (mA) | Inhibition Efficiency (%) |
|-------------------|----------|------------|---------------------------|
| 0                 | -0.39    | 1.91×10⁻⁴  | -                         |
| 2                 | -0.385   | 1.35×10⁻⁴  | 29.20                     |
| 4                 | -0.41    | 9.5×10⁻⁵   | 49.88                     |
| 6                 | -0.42    | 7.59×10⁻⁵  | 60.19                     |
| 8                 | -0.37    | 6.03×10⁻⁵  | 68.38                     |
| 10                | -0.38    | 3.8×10⁻⁵   | 80.05                     |

Table 1 shows that steel immersed in 0.75 M H₂SO₄ without CBHE (0 g/L) has a current of 1.91×10⁻⁴ mA while in the presence of CBHE with concentrations of 2, 4, 6, 8, 10 g/L respectively has a current of 1.35×10⁻⁴, 9.5×10⁻⁵, 7.59×10⁻⁵, 6.03×10⁻⁵, and 3.8×10⁻⁵ mA. This data explains that steel immersed in the absence of CBHE has a higher current than the presence of CBHE. This is caused by the formation of layers on the surface of mild steel, thus inhibiting the flow of electrodes. The greater the CBHE concentration, the lower the current value. The inhibition efficiency of 10 g/L CBHE in a 0.75 M H₂SO₄ solution was 80.05%. The inhibitory efficiency values obtained by the weight loss method differ from the potentiodynamic method due to differences in the absorption time of CBHE molecules on the mild steel surface. Corrosion potential value (Ecorr) in steel immersed in 0.75 M solution without CBHE was -0.39 V while in the presence of CBHE 4 and 6 g/L respectively -0.41 and -0.42 V had Ecorr more negative than Ecorr without CBHE and CBHE concentrations of 2, 8 and 10 g/L each had Ecorr of -0.385, -0.37 and -0.38 more positive than Ecorr in the absence of CBHE. The more negative shift from Ecorr in the absence of CBHE (blank) is called a cathodic inhibitor meaning it inhibits the hydrogen evolution reaction. The more positive shifts in Ecorr blanks are called anodic inhibitors. Anodic inhibitors inhibit the dissolution of anodes from iron [12]. If the Ecorr value shifts in the positive and negative direction of the Ecorr blank, it is called a mixed inhibitor [13]. CBHE as a corrosion inhibitor in steel in 0.75 M H₂SO₄ is a mixed inhibitor.

3.3. Fourier Transform Infra-Red Analysis

The results of the CBHE IR spectrum in Figure 3a show the presence of an OH functional group in the presence of an absorption peak at a wavenumber of 3275.08 cm⁻¹. Peaks at wavenumber of 2933.55 cm⁻¹ indicate the presence of C-H metal bonds and methylene groups, and are supported by the presence of C-O bonds at wavenumber of 1235.34 cm⁻¹ and 1028.33 cm⁻¹. Peak C = C at wave number absorption 1640.17 cm⁻¹ and at wavenumber of 501.16 cm⁻¹ there are aromatic C-H bonds.

Figure 3b is a spectrum of layers formed on a steel surface and shows a shift in the number of waves OH group at wavenumber 3275.08 cm⁻¹ shifted to 3158.59 cm⁻¹, group C = C shifted from 1640.17 cm⁻¹ to 1632.98 cm⁻¹, CO group shifted from 1235.34 cm⁻¹ to 1077.88 cm⁻¹ and a wavenumber of 466.71 cm⁻¹. The spectrum shows the peak that emerges from the coating on the steel surface is the peak of the group containing CBHE which can act as a corrosion inhibitor and has been adsorbed on the steel surface.
Figure 3. a) CBHE extract, b) The surface layer of steel after immersion with CBHE for three days in 0.75 M sulfuric acid solution

3.4. Scanning electron microscope analysis
Scanning Electron Microscopy (SEM) analysis provides information on the morphological shape of the mild steel before treatment, after immersion in 0.75 M sulfuric acid for 72 hours, and after immersion in a 10 g/L CBHE inhibitor solution for 72 hours. Figure 4a shows the surface morphology of mild steel without treatment at 1000× magnification, the surface of the mild steel looks good because there is no interaction with the corrosive medium.

Figure 4b shows the surface of the mild steel has undergone corrosion and damage on the mild steel surface. The surface of mild steel looks rough, uneven, and there are holes due to corrosion by sulphuric acid. Figure 4c shows that the surface of mild steel is less damaged than the surface of steel immersed in a corrosive medium without CBHE. This occurs because secondary metabolites contained in CBHE adsorbed on the surface of mild steel form a thin layer so that the mild steel surface becomes protected and can inhibit the rate of corrosion [13]. Figure 4c shows the mild steel surface protected by adsorption of CBHE which has inhibited the corrosion rate so that the corrosion rate obtained is very small at 0.213 mg/cm² hours in 72 hours immersion seen in Figure 4.
Figure 4. SEM results of mild steel: a) blank; b) immersion in 0.75 M sulfuric acid for 72 hours; c) immersion in CBHE 10 g/L for 72 hours

4. Conclusion
Coffee bean extract can inhibit the rate of corrosion of mild steel in sulphuric acid media by 97.543 % at a concentration of 10 g/L and soaking for 72 hours in the weight loss method and 80.05 % in the potentiodynamic polarization method. Coffee bean husks extract used as a mild steel corrosion inhibitor in H₂SO₄ corrosive medium is a mixed type inhibitor. Therefore, it inhibits the dissolution of iron at the anode and the evolutionary reaction of hydrogen at the cathode.

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