Corrosion inhibition using lignin of sugarcane bagasse

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Abstract. The quality of ferrous metals may decrease due to corrosion. The corrosion rate can be inhibited using inhibitors derived from organic compounds. Sugar cane waste from the sugar industry contains lignin that can be used as an environmentally friendly organic inhibitor, also called green inhibitor or eco-friendly inhibitor. The present article describes the use of green eco-friendly lignin natural polymer as corrosion inhibitor on the surface of ferrous metal in acidic media. Lignin was isolated from bagasse by acidification methods and characterized by FTIR to confirm the functional groups. The inhibition effectiveness of lignin against corrosion rate was observed by varying the concentration of lignin and metal immersion time in acidic medium. By using weight-loss method, it was found that the optimum inhibition effectiveness was 80.79% using the lignin concentration of 10 g/L and metal immersion time for 6 hours. The corrosion rate decreases with increasing lignin concentration of bagasse and length of immersion time.

1. Introduction
Corrosion is deterioration of metals due to spontaneous electrochemical reactions. Deterioration or destruction of metals is an unavoidable event yet controllable process. Many investigations were conducted to inhibit the corrosion process [1,2].

Organic inhibitors are more developed and used than inorganic inhibitors because they are more environmentally friendly, safe, practical, low cost and renewable [3]. Organic inhibitors known as green inhibitors or eco-friendly inhibitors. Many organic inhibitors derived from natural sources such as plants were flavonoids, alkaloids, or other natural products [2].

Bagasse is usually utilized as an alternative energy sources such as bioethanol or biogas, because it contains 52.7% cellulose, 20.0% hemicellulose, and lignin 24.2% [4,5]. Relatively high lignin content in the bagasse is potential to be used as a corrosion inhibitor [6]. Lignin is a phenolic macromolecule [7] consists of the three main phenylpropane units (monoglinol), i.e. coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. The functional groups in lignin are phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxy and aldehyde that make lignin useful as a corrosion inhibitor. The functional group contains double bonds and free electron pairs on the O atoms which enable lignin to be adsorbed on the metal surface forming a barrier between the metal and the corrosive environment [8].

The potential of lignin as a corrosion inhibitor has been investigated by Altwaiq, et al. [8]. Alkali lignin was extracted from sawdust of a maple wood tree. Alaneme and Olusegun [9] also have investigated the inhibition potentials of lignin extract from sunflower. Study of the use of lignin from the skin of coffee as an inhibitor performed by Hasan, et al. [10]. Isolation of lignin from sugarcane bagasse was once performed by Lubis, et al. [11], but there was no utilization of the isolated lignin as corrosion inhibitor.
In this paper, we reported a study of lignin utilization from sugarcane bagasse as a corrosion inhibitor with variation of lignin concentration and immersion time.

2. Method

Materials and tools used in this research were bagasse as lignin source, iron plate, hydrochloric acid 37%, sodium hydroxide 10%, glassware, analytical balance, sandpaper, filter paper, vacuum, 40 mesh sieve, oven, grinding machine and FTIR spectrometer. Pre-treatment of iron plate was carried out by grinding the iron plate surface with sandpaper, rinsing with distilled water, degreased with acetone then dried in the oven at 45 °C for five minutes. After that the iron plate was weighed by the analytical balance to determine the initial weight (W₀).

Isolation of lignin from bagasse was done through several stages. The bagasse was dried, made into powder, filtered using a 40 mesh sieve and then treated with sodium hydroxide solution (solid-liquid ratio 1:10) at 170 °C for 1 hour. After treatment, the mixture was cooled for 2 hours and then filtered. Hydrochloric acid solution was added to the filtrate solution until pH 2 was reached in order to precipitate the lignin. The lignin precipitate was cooled in freezer for 24 hours, air dried and filtered using vacuum filter while washed with distilled water. The lignin residu was heated in the oven at 45°C for 24 hours. The lignin was then weighed and characterized FTIR spectrometer.

Iron plate is immersed in lignin solution at varying concentrations of 5, 10 and 10 g/L and fed into a corrosive medium containing 50 ml of 1 M HCl solution with immersion time of 2, 4 and 6 hours. After immersion, the iron plate was washed, dried in the oven, and weighed. The corrosion rate (CR) was calculated by weight-loss method using equation (1). Percent inhibition efficiency (%IE) was calculated using equation (2) where CR₁ was corrosion rate in corrosive medium at zero concentration of lignin.

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CR = \frac{\text{Initial Weight of iron (g)} - \text{Weight of corroded iron (g)}}{\text{exposed area (cm}^2) \times \text{exposure time (hour)}}
\]

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%IE = \frac{\text{CR}_1 - \text{CR}_2}{\text{CR}_1} \times 100\%
\]

3. Result and discussion

3.1. The isolation and characterization of lignin

In lignin isolation, dry sugarcane bagasse which has been filtered using a 40 mesh sieve was dissolved in sodium hydroxide solution, thus forming a soluble phenolic salt [10]. To accelerate the formation of a phenolic salt and separating the lignin from the other compounds, heating at 170°C was carried out on the mixture. Such treatment produces black liquor containing lignin and residue waste. After filtration, the black filtrate is acidified using HCl to pH 2, so that lignin precipitates. Precipitation until pH 2 is performed to maximize lignin precipitation [12]. Addition of acid will change the phenolic salt of lignin into lignin neutral base that cannot be dissolved in water [13]. By filtration, lignin is separated and then heated in an oven at a temperature of 45 °C to obtain lignin in solid form.

Analysis of the functional groups of lignin using FTIR spectrometer was performed by direct transmission using potassium bromide (KBr) pellet technique. FTIR spectrum was recorded in the range of 4000 to 400 cm⁻¹. Resulting of IR spectrum of lignin can be seen in Figure 1. These results have been compared with the results of FTIR analysis from Lubis et al. [8] research. Tabulation of data from absorption bands of lignin compared to absorption bands of standard lignin [14] is shown in Table 1. These results indicate that the FTIR spectrum of lignin isolated from bagasse is similar with bagasse lignin from Lubis, et al [11].
Table 1. Comparison of IR absorption bands of bagasse and standard lignin.

| Absorption Bands (cm⁻¹) | Lignin of sugarcane bagasse | Standard Lignin [14] | Functional groups |
|-------------------------|-----------------------------|----------------------|------------------|
| 3447,104                | 3400-3450                   | O-H stretch          |
| 2927,405                | 2820-2940                   | C-H stretch          |
| 1636,390                | 1600-1650                   | C=C Aromatic        |
| 1506,846                | 1505-1515                   | C=C Aromatic        |
| 1459,276                | 1460-1470                   | C-H asymmetry        |
| 1389,245                | 1350-1400                   | C-O stretch          |
| 1067,347                | 1030-1085                   | C-H Aromatic        |

Figure 1. IR spectrum of lignin of sugarcane bagasse.

3.2. The effectiveness of lignin bagasse as a corrosion inhibitor

The effectiveness of lignin as corrosion inhibitor was measured by immersing the iron plate in lignin mixture with 1 M HCl (as corrosive medium). The variations of lignin concentration used were 5 g/L, 10 g/L and 15 g/L and immersion time of 2, 4 and 6 hours. From these experiments we obtain the masses of iron plate before and after immersion in corrosive media. The data is used to determine the corrosion rate using weight-loss method.

The effect of lignin concentration and immersion time on corrosion rate can be seen in Figure 2. From the graph (Figure 2), it is known that the higher concentration of lignin bagasse and the longer immersion time of iron plate generally results in the decreasing of the corrosion rate. According to Sighk and Mukherjee [15] the decrease in corrosion rate against increased time occurs due to the formation of a passive layer from the accumulation of corrosion products on metal surfaces so that the corrosion rate decreases.

The most optimal conditions of lignin as an inhibitor were obtained at lignin concentration of 10 g/L with 6 hours immersion time. Based on the calculation using equation (2), it is known that the efficiency of lignin inhibition on the addition of lignin concentration of 10 g/L and the immersion time of 6 hours is 80.79%, while the lowest efficiency reached in the addition of lignin concentration of 5 g/L at immersion time of 2 hours which is about 7.96%. The findings from this study tend to be similar to the results of research conducted by Hasan, et al. [10].
The inhibitory effect of corrosion rate by lignin associated with functional groups as revealed by the results of the analysis using FTIR spectrometer [13]. Lignin adsorbed on the metal surface forming a barrier between the metal and the corrosive environment. In addition, lignin has a high surface area (180 m² g⁻¹) that exhibits surface activity [8]. The findings in this study also reinforce the importance of exploring potential natural materials as environmentally friendly organic inhibitors [2].

4. Conclusion
The yield of lignin from bagasse was 15.4% and FTIR analysis showed that lignin contain double bonds and OH groups which in O atoms have free electron pairs. The greater variation of lignin concentration and the longer the immersion time of the metal may decrease the corrosion rate, since lignin adsorbed on the metal surface to form a barrier layer between the metal and the corrosion environment. The optimum inhibition effectiveness is 80.79%.

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