Recovery of nano-lignin from anaerobic treated palm oil mill effluent (AT-POME)

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Abstract. Lignin is the main polymers in woody biomass aside cellulose and hemicelluloses. Recently, nano-lignin is gaining importance due to the increasing demand for bio-based and bio-active nanomaterial fillers for many applications such as in composite and textile industries. Palm oil mill effluent (POME) is the main wastewater produce by palm oil mills. Anaerobically treated (AT-POME) contains high soluble lignin due to the anaerobic digestion of cellulosic material in POME. Nano-lignin was precipitated by adjusting the initial pH of AT-POME during the sonication process. Sulfuric acid (H₂SO₄), nitric acid (HNO₃), hydrochloric acid (HCl) and phosphoric acid (H₃PO₄) were used to adjust the initial pH of AT-POME. Result shows that sulfuric acid was the most suitable acid to be used as it could recovered 96% of the soluble lignin in AT-POME. The presence of ultrasonic during the precipitation process had reduced the size to 383.4 nm. The optimum operating parameter for lignin recovery is at pH 4 using sulfuric acid and sonicated at 80 watts for 15 minutes. This study shows that sonication could reduce the size of precipitated lignin from AT-POME. In addition, removal of lignin from AT-POME also reduced the COD content of AT-POME.

1. Introduction

Malaysia is one of the largest producers and exporters of palm oil in the world. The production of palm oil resulted in huge volume of wastewater known as palm oil mill effluent (POME). POME is a brown colloidal solution with high COD and BOD contents. POME also contain high total suspended solid (TSS) which most of them are cellulosic materials.

In most mills, anaerobic digestion method is used to treat POME as it is very effective and economical way to treat wastewater with high COD content. Since lignin is very hard to digest by the microbes compared to cellulose and hemicelluloses, lignin remains in POME [1]. The presence of soluble lignin makes the AT-POME looks darker compared to raw POME.

Recently, great interest has grown up on the potential use of modified lignin as an alternative source of renewable energy as well as ‘green material’ in many applications. Lignin has the highest combustion heat energy among natural polymeric compounds that contain carbon, hydrogen and oxygen [2]. Blending lignin with polyolefins will giving UV stabilization [3][4]. Renewable resin can be produced when lignin is blended with PLA [5]. Lignin can also act as antimicrobial and antioxidant material [6, 7, 8], additive in fertilizer [9] and drilling fluid [10].

Acidification of raw AT-POME could precipitate soluble lignin as reported by Sun & Tomkinson [11]. Due to ultrasonic cavitation effect, the size of precipitated lignin from AT-POME could be
reduced up to nano size material. As lignin present in a very small size, it would improve the solubility and its functionality hence open many benefits and create new applications. 

In this research, we studied the effect of different type of acid on the volume of recovered lignin. We also study the effect of sonication on the size of precipitated lignin produced from AT-POME.

2. Materials and methods

2.1. Materials and chemical

AT-POME used in this study was collected from the outlet of anaerobic digestion pond at Malpom Sdn. Bhd, Nibong Tebal, Penang, Malaysia. Sulfuric acid (H2SO4), nitric acid (HNO3), hydrochloric acid (HCl) and phosphoric acid (H3PO4) used in this study was supplied by R&M Chemicals.

2.2. Characterization of AT-POME

AT-POME collected from the site was characterized to determine its COD, TSS, colour and lignin content. COD, colour and lignin content was tested using HACH method 8000, 8271, 8025 and 8193 respectively.

2.3. Lignin recovery

Raw AT-POME was centrifuged at 2500 rpm for 10 minutes to separate the particles in the solution. pH of raw AT-POME adjusted to pH 2, 3, 4, 5 and 6 using different type of acid (H2SO4, HNO3, HCl and H3PO4). AT-POME was placed on the shaking plate for 10 minutes to allow the soluble lignin to precipitate. Next, AT-POME was centrifuged again to separate the precipitated lignin from the solution. The final COD, colour and lignin content inside the AT-POME was recorded. Lignin recovered from AT-POME was calculated as:

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\text{\% Lignin recovered} = \frac{\text{Soluble lignin (initial) - Soluble lignin (final)}}{\text{Soluble lignin (initial)}} \times 100
\]  

(1)

2.4. Sonication effect of lignin size

AT-POME which has been pH adjusted was sonicated at different power intensity at different reaction time. Power intensity used for sonication were 40, 60 and 100 watts while the reaction time were 5, 10 and 15 minutes. After the reaction time ended, the solution was tested using Zetasizer Nano ZS to determine the size of the precipitated lignin.

3. Results and discussions

The COD reading of raw AT-POME was 1412 mg/L. Meanwhile, the pH of AT-POME was recorded as 8.23. This may due to the addition of sodium hydroxide (NaOH) or potassium hydroxide (KOH) at initial stage of anaerobic digestion process of AT-POME. Table 1 shows the summary of AT-POME characteristics.

The colour of AT-POME is darker compared to raw POME. This was due to the high amount of tannin and lignin in AT-POME, resulted from the digestion process of lignocellulosic biomass in raw POME. Since lignin was not digest by the microorganism, it remains inside the AT-POME as soluble lignin. Recorded soluble lignin in AT-POME was 224 mg/L.

Sample of AT-POME was added with 0.5 mol of either sulphuric acid (H2SO4), nitric acid (HNO3), hydrochloric acid (HCl) and phosphoric acid (H3PO4). These acids were added to change the pH of the AT-POME samples. The pH changed from 8.23 to pH 2, 3, 4, 5 and 6. Figure 1 shows that the colour changes of AT-POME sample after being added with H2SO4.
Table 1. Characteristics of raw AT-POME.

| Parameters                  | Result         |
|-----------------------------|----------------|
| COD                         | 1412 mg/L      |
| Colour (true)               | 249 PtCO       |
| Total Suspended Solid (TSS) | 314 mg/L       |
| pH                          | 8.23           |
| Soluble Lignin              | 224 mg/L       |

Figure 1. Colour of AT-POME at different pH (from left: pH 2, 3, 4, 5 and 6).

As the pH decreases, the colour of AT-POME also became clearer than the raw sample. Less volume of acid was needed to adjust the pH when strong acid such as H$_2$SO$_4$ was used compared to HNO$_3$. In addition, strong acids also dissociate completely in water at a moderate concentration. Result shows that H$_2$SO$_4$ was the best acid to be used during acidification process of AT-POME where 96% of soluble lignin could be recovered as shown in Figure 2.

Figure 2. Lignin recovery using different type of acid at different pH.

Even though HCl is the strongest acid, H$_2$SO$_4$ may suitable react with lignin thus produce the highest result of lignin recovery. The best pH was pH 4. This is reasonable since more phenolic groups are protonated at a higher concentration of hydrogen ions (i.e. lower pH). The protonation of phenolic groups in lignin leads to a decrease in the electrostatic repulsion between lignin consequently, the lignin molecules become less hydrophilic and the solubility of lignin is reduced.

Ultrasonication is a process to break the precipitated lignin into smaller size particles. In this study, pH 4 and pH 3 were chosen for ultrasonication process. This is because both pH recovers maximum
amount of lignin which are 96% and 93%. Based on result in Figure 3 and Figure 4, the highest lignin recovery from pH 4 and pH 3 after 15 minutes of 80watt sonication process were 62% and 88% respectively. Result also shows that by increasing the power intensity and prolong the reaction time, more lignin can be recovered from the sample.

![Figure 3. Sonication process of AT-POME at pH4 with different energy intensity.](image)

![Figure 4. Sonication process of AT-POME at pH3 with different energy intensity.](image)

Zetasizer Nano-ZS was used to identify the nano-lignin particles in the sample that already undergoes sonication process. The smallest size of lignin was 383.4 nm which from pH 4 at 80-watt in 15 minutes reaction time as shown in Figure 5. This shows that pH 4 is the best pH that obtain the smallest size of precipitated lignin.

![Figure 5. Size of precipitated lignin subjected to sonication process.](image)

Removal of lignin from the solution also improved the quality of AT-POME. COD of AT-POME sample was reduced rapidly after the acidification treatment. Similar effect was reported by Ibrahim et al. [12]. It became better after ultrasonication process was applied to the sample. As results, the COD change from the original which was 1412 mg/L to the lowest COD in pH 4 was 833 mg/L. While the colour of AT-POME also reduced to 116 PtCo after being sonicated at 40-watt for 5 min at pH 3.
4. Conclusion

Acidification of AT-POME will precipitate the soluble lignin inside the solution. Volume of acid used can be minimized when strong acid such as H$_2$SO$_4$ is used. Sonication of AT-POME after pH adjustment would result in smaller size of precipitated lignin. Besides lignin recovery, removal of lignin would also improve the quality of AT-POME by reducing the COD and colour of the wastewater.

Acknowledgement

The authors would like to thank the Ministry of Education, Malaysia for funding this research under Fundamental Research Grant (FRGS 9003-00477). We also would like to thank Universiti Malaysia Perlis (UniMAP) for their financial support.

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