Study on Bamboo Sawdust Structure Breakage on Manganese Leaching Application

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Abstract. The purpose of this work is to study Bamboo Sawdust (BSD) structure breakage to assess its use as potential reducing agent in manganese leaching application. The determination of holocellulose, cellulose and hemicellulose was carried out using BSD reaction towards acetic acid and sodium chlorite (NaClO₂). Afterwards, the residue reacted with acetic and nitric acid. Result shows BSD contents 28.60% hemicellulose, 84.71% holocellulose and 56.11% cellulose. During the holocellulose analysis formation of pores was observed. This indicated degradation of holocellulose into reducing sugars. Meanwhile, cellulose analysis caused BSD bundles isolated into individual component. The treatment generates degradation of cellulose into reducing sugars. In addition, the suitability of BSD as a reducing agent is also investigated. In this part, raw BSD undergone leaching reaction and the residue structure was determined using Field Emission Scanning Electron Microscope (FESEM). Two type of manganese (Mn) ores were analysed which were Low Grade Manganese Ore (LGMO) and Synthetic Manganese Ore (SMO). As a result, leaching with manganese ores in sulphuric acid solution develop pores on BSD structure illustrate degradation of BSD into reducing sugars. In addition, the recovery reveals Mn was extracted up to 70% for LGMO and 95% for SMO within 120 minutes of reaction. Accordingly, BSD capable released cellulose as reducing agent hence suggests BSD is suitable reducing agent to extract manganese ore.

1. Introduction
Bamboo is a renewable woody grass and often used to replace wood [1]. It is easily cultured in tropical and subtropical zone [1-2]. Some of the bamboo species are Gigantochloa Levis, Gigantochloa Wrayi and Gigantochloa Brag. The most common species is known as Buluh Semantan (Gigantochloa Scortechinii) that grows abundantly in Peninsular Malaysia [4-5].

Bamboo cell wall composed of 90-98% cellulose, hemicellulose and lignin. The remaining 2-10% of bamboo cell wall composed of extractive. Cellulose presents in bamboo is a long chain polymer of glucose and the configuration is differs from starch [5]. The degradation of cellulose produces oligosaccharides which are cellotetraose, cellotriose and cellobiose and monomeric sugars which are glucose and fructose [1]. Meanwhile, amorphous hemicellulose configuration is branched polymers of five carbon sugars (pentoses). Generally, hemicellulose degrades into pentose sugars such as xylose and arabinose [1]. These sugars are normally helps in reducing metals particularly manganese dioxide (MnO₂). They function as a reducing agent to reduce metals into lower form [9–12].

Previous researches had studied acid treatment to identify cellulose, hemicellulose and holocellulose of bamboo sawdust [3–5], [10–13]. However, most of the research works focused on bamboo composites, cellulose fibres and pulp production. For example, Cao et al., 2014 in his works...
studied characterization of bamboo to produce pulp production and Parnia et al., 2014 studied preparation of bamboo fibre reinforced composites [10, 12]. Besides that, there are some works described on characterization of bamboo and bamboo in leaching application [3–5], [14]. However, none of these researchers studied on the structure breakage of bamboo sawdust on leaching application.

Therefore, this work aims to study BSD structure breakage to assess its use as potential reducing agent in manganese leaching application. Thus, FESEM was utilised to study the BSD structures before and after chemical treatments. The structures are observed and described. Amount of cellulose, hemicellulose and holocellulose in the BSD are calculated. In addition, the suitability of BSD as a reducing agent is investigated. BSD structures changes after leaching is described. The reduction of Mn ore using BSD as a reducing agent is discussed.

2. Materials and Methods

2.1 Raw materials and chemicals

Bamboo sawdust was obtained from Forest Research Institute Malaysia (FRIM). The type of BSD used was Gigantochloa Scortechinii. The bamboo part used was culm. The bamboo was washed, dried, cut and ground until -75μm size was achieved. The ash content and extractive analysis of BSD were 3.37% and .

LGMO was obtained from Pahang, Malaysia. The ore was dried, ground and sieve to achieve -75μm. Elemental content of the ore consist of 15.26% Mn, 4.05% Fe, 2.74% Si and 2.71% Al. Phases present in the ore were pyrolusite, MnO$_2$ (ICDD card no. 98-006-2906), goethite, FeO(OH) (ICDD card no. 98–003-4797) and quartz, SiO$_2$ (ICDD card no. 98-010-7202) [15].

SMO was obtained from Acros Organics (99%, -10 mesh). Ore was sampling and ground into -75μm. The elemental content of SMO was 34.33% Mn and phase present in this ore was pyrolusite, MnO$_2$ (ICDD card no. 98 003 5167).

Chemicals used include 95%-97% sulphuric acid, 100% acetic acid, 65% nitric acid, 95% ethanol, acetone, 99% EDTA, thmolphatalexone indicator and silicone oil. All chemicals used are analytical grade. Dilution was made using deionized water.

2.2 Hemicellulose, holocellulose and cellulose content of BSD

Holocellulose identification was performed in 100mL conical flask. Approximately 1g of BSD samples were hydrolyzed with 30mL deionized water, 0.08mL acetic acid and 0.8g NaClO$_2$ for an hour at 75°C. After an hour, 0.08mL acetic acid and 0.4g NaClO$_2$ were added. Same amount of acetic acid and NaClO$_2$ were added every hour for 3 hours respectively. Then, residue was filtered, washed using deionized water and acetone and dried at 60°C. The final weight of holocellulose was taken.

Cellulose identification was carried out using dry solid residue from previous final holocellulose analysis. The residue was mixed with 3mL of reagents mixture (80% acetic acid and 70% nitric acid). The reagent ratio was 10:1. The mixture was heat at 100°C for 2 hours in oil bath. Later, mixture was cooled down and 60mL deionized water was added. The mixture was filtered, washed with deionized water and dried at 60°C. The final weight of cellulose content was recorded. Equation 1 to Equation 3 indicates hemicellulose, holocellulose and cellulose calculation.

\[
\text{Hemicelluloses} \% = \text{Holocellulose} \% - \text{Cellulose} \%
\]

\[
\text{Holocellulose} \% = \left[\frac{\text{Weight initial} - \text{Weight final}}{\text{Weight final}}\right] \times (100\text{- extractives} \%)
\]

\[
\text{Cellulose} \% = \left[\frac{\text{Weight initial} - \text{Weight final}}{\text{Weight initial}}\right] \times (100\text{- extractives} \%)
\]
2.3 Leaching of LGMO and SMO using BSD as a reducing agent

In this work, BSD application as a reducing agent to extract Mn ore was analyzed. Two types of ores were used which were LGMO and SMO. Reductive leaching was performed in 500mL three neck flask immersed in silicon oil bath. The reactor was connected with condenser and thermometer was placed inside the glass reactor and at silicon oil bath to measure the temperature.

25g of Mn ore (LGMO or SMO) size -75μm was added into 4M of 250mL sulphuric acid at 100°C. Later, 7.5g of raw BSD (-75μm) was poured in reaction flask. The solution was stirred at 300rpm and leaching was continued until 360min.

2mL sample was withdrawn during leaching process at 15min, 60 min, 120 min, 240 min and 360 min. These samples were filtrate using Whatman, Kent, UK, 0.45 um (GMF- PTFE). Mn determination was determined using complexometric titration with EDTA as a titrant. Meanwhile solid residue was undergone SEM observation to identify BSD structure breakage.

3. Results and Discussion

3.1 Hemicellulose, holocellulose and cellulose content of BSD

The function of this analysis was to determine holocellulose, cellulose and hemicellulose content in BSD. The finding indicated BSD contents 28.60 % hemicelluloses, 84.71 % holocellulose, and 56.11 % cellulose. These contents were coherent with previous researchers which reported holocellulose content in BSD was in the range 65.91% to 82.3% and cellulose was between 38.96% to 64.6% [3–5]. This high holocellulose, cellulose and hemicellulose content have high tendency to degrade into reducing sugar to extract Mn ore.

3.2 Structure identification of BSD using FESEM analysis

3.2.1 Structures of raw BSD. The observation of BSD under FESEM was performed to understand the structure surface of BSD. Figure 1 shows the structure of raw untreated BSD observed by FESEM.

Figure 1. Hollow cylinder structure of BSD

Figure 1 display the structure of BSD was in hollow cylindrical shape. The cell wall was in rigid structure. Besides that, the structured showed the culm was rough and uneven.

In addition, bamboo composed of several vascular bundles. The function of these vascular bundles was to provide strength to the culm [10]. Generally, vascular bundles consist of fibre strand. This fibre strand contents lignin and hemi-cellulose. Figure 2A and Figure 2B display the vascular bundle meanwhile Figure 2C and Figure 2D display the fibre strand of BSD.
3.2.2 Structures of holocellulose and cellulose analysis of BSD. Meanwhile, holocellulose analysis produces rougher BSD structures. The BSD was no longer rigid. The study developed formation of pores in the BSD structure. These pores indicate the holocellulose had been degraded into reducing sugars. A lot of pores present in the BSD after the reaction between acetic acid and sodium chlorite analysis. The generation of numerous pores supported with the result of high holocellulose content in BSD. High yield of holocellulose degraded into reducing sugars. Figure 3A and Figure 3B reveals the formation of pores in BSD structure after pretreatment with acetic acid and sodium chlorite at 75°C. Meanwhile, Figure 3C and Figure 3D expressed the FESEM of BSD structures after cellulose analysis.

3.3 Application: Leaching of LGMO and SMO using BSD as a reducing agent

Generally, Mn does not exist as a free element in nature. It often combines with other elements such as oxygen and iron. The common ore of Mn is pyrolusite (MnO₂) [16]. This Mn (IV) oxide has limited value in the industry [17]. Hence, it needs to reduce into Mn (II) or Mn metal to make it commercial in industry like iron and steel making.

Previous research had studied reduction of Mn (IV) in the absent of reducing agent. The research found out Mn was unable to reduce without the presence of reducing agent [18]. Therefore, this work utilized raw BSD as a reducing agent to reduce Mn ore. The leaching was made using diluted sulphuric acid (4M) instead of high acid concentration. Raw BSD was used to determine the BSD structure changes without pretreatment analysis.

It was found out Mn was successfully reduce into Mn (II) in the presence of BSD as a reducing agent. Figure 4 illustrates FESEM of BSD structures after leaching process. Figure 4A indicates the cell wall of BSD becomes rougher compared to raw BSD. Besides that, the images shown revealed BSD was not fully break out but there were some formation of pores develops in the BSD structures.
The formation of pores develops in both leaching of LGMO ore and SMO which was seen in Figure 4B and Figure 4C. This expressed the diluted acid reaction occurred during leaching process able to degrade BSD into reducing sugars. In addition, based on the observation of FESEM analysis the ore was accumulated around BSD structures. These shows there were reaction occurred between ore and BSD in sulphuric acid.

![BSD structure after leaching](image)

Figure 4. BSD structure after leaching

Further, the recovery reveals Mn was extracted up to 70% for LGMO and 95% for SMO within 120 minutes of reaction. This indicates the suitability of BSD as a reducing agent to reduce Mn ore using diluted sulphuric acid. Figure 5 shows the reduction of Mn ore using BSD as a reducing agent in sulphuric acid.

![Mn extraction using BSD as a reducing agent](image)

Figure 5. Mn extraction using BSD as a reducing agent

4. Conclusion
This work aims to determine BSD structure breakage to assess its use as potential reducing agent in manganese leaching application. The treatment of BSD with acetic acid and sodium chlorite at 75°C developed formation of pores in the BSD structure. These pores indicate the holocellulose had been degraded into reducing sugars. In addition, BSD structure becomes rougher. Further treatment analysis using acetic and nitic acid caused some part of vascular bundles separated into individual components. This indicates cellulose had been degraded into reducing sugars. The treatment also indicates BSD contents 28.60 % hemicelluloses, 84.71 % holocellulose, and 56.11 % cellulose.

In addition, the suitability of BSD as a reducing agent is also investigated. LGMO and SMO were reduced using BSD as a reducing agent in H_2SO_4. The reaction shows formation of pores develops in both leaching of LGMO ore and SMO. This revealed acid reaction occurred during leaching process able to degrade BSD into reducing sugars.

The result was supported with Mn was extracted up to 70% for LGMO and 95% for SMO within 120 minutes of reaction. This indicates the suitability of BSD as a reducing agent especially to reduce Mn ore.
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