Morphology and structure of sawdust waste after adding magnetic nanoparticles

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Abstract. Sengon (Albizia chinensis) is a type of forest plant that grows quickly and is widely used to meet human needs. The large number of uses of Sengon wood causes sengon wood waste, such as sawdust, to increase. The study's aim is to analyze the morphology and structure of sawdust waste after adding magnetic (Fe3O4) nanoparticles. The methods include collecting sawdust waste from wood (Sengon) was conducted by the crushing process to get smaller sawdust sizes. Alkalization was applied to sawdust and followed by a bleaching process. The powder is then immersed in a solution containing magnetic (Fe3O4) nanoparticles of 10wt%, and then dried. Sawdust composite powder the analyzed using X-ray diffraction and electron microscope instruments. The result indicates that magnetic nanoparticles deposit on sawdust powder and then make the powder become rougher. Higher content of magnetic nanoparticles causes higher agglomeration. The diffraction pattern with 2θ of 14, 16, and 22□ indicates that the structure of sawdust is cellulose 1β. The degree of crystalline of sawdust powder reduces from 76.1% to 73.3% after adding magnetic nanoparticle. In the future, these composite powder results will develop as flocculants for wastewater treatment.

1 Introduction

The majority of cellulose, which is the Earth's most abundant biopolymer, is sourced from wood pulp, and it is anticipated to achieve an estimated market worth of about USD 48.37

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billion by 2025 [1]. In 2019, Indonesia's log production achieve 48.0 million cubic meters [2]. Given that there are an estimated 2 million cubic meters of sawdust generated annually [3], sawdust emerges as a promising resource for cellulose production. Natural cellulose fibers have many advantages because of cheap, available abundantly, and eco-friendly materials [4].

Some researchers have explored the utilization of sawdust as a cheap flocculant/absorbent [5, 6]. Nevertheless, the challenge lies in the intricate and time-consuming process of separating sawdust-based flocculants from treated wastewater [7]. Additionally, cellulose's relatively low charge density on its surface can affect its dye adsorption capabilities [8]. However, it's worth noting that natural polymers like cellulose biodegrade over time, leading to decreased stability and strength in floc formation during coagulation-flocculation process [9]. They also exhibit reduced efficiency [10]. To enhance cellulose's performance in flocculation, researchers have pursued chemical functionalization on the surface of cellulose using copolymerization [11, 12]. Another approach involves incorporating particles like MoS_2 [13].

In recent times, there has been a growing interest in the advancement of cellulose composites. These composites, when strengthened with nanoparticles, have the capacity to modify the properties of the composite material to get unique functionalities. One such enhancement involves conferring hydrophilic properties through the use of magnetic nanoparticles, specifically Fe_3O_4 nanoparticles. These nanoparticles facilitate the chemical interaction among oxygen with hydroxyl groups which have surplus electrons [14]. Additionally, the attractive force between the cellulose fibril and magnetic nanoparticles generates another intramolecular interaction. Moreover, the incorporation of mechanical interlocking serves to further restrict the cellulose fibrils movement by magnetic nanoparticles, consequently bolstering the strength of the resulting nanocomposite [15, 16]. Notably, Magnetic nanoparticle systems have demonstrated their ability to efficiently inhibit communities of fecal coliform and enterococci bacteria [17], as well as enhancing the charge capacitance capacity of cellulose material [18]. Efforts are being made to functionalize magnetic nanoparticles from sawdust when applied as a wastewater flocculant or coagulant for easier separation using a magnet. Therefore, the aim of the study is to investigate the morphology and structure of sawdust powder derived from wood after the reinforcement of magnetic nanoparticles.

2 Methods

2.1 Materials

The sawdust waste was collected from Sengon (A.chinensis) wood in Malang, Indonesia. Chemical treatment used H_2O_2 (Merck, Singapore), NaOH (Merck, Singapore), and magnetic nanoparticles (Fe_3O_4) (Hongwu Materials Tech., Cina).

2.2 Chemical treatment

The process begins by crushing sawdust waste into a powdery form, which takes approximately 10 minutes. Following this, sawdust powder of 100 g is soaked in the water of 4 L for 5 days, with the circulation of new water every day to remove materials dissolved by the water. Next, sawdust powder was oven-dried at a temperature of 110-120°C for 20 h. Each 4 g of sawdust was then subjected to an alkalization process using 80 mL of NaOH with a concentration of 5%. This process was conducted for 3 h on a hotplate set at a temperature of 180°C. The powder is subsequently washed four times and immersed for 3 h with 500 mL

of distilled water. This process was repeated four times. Next, a mixture is prepared consisting of 10% dry sawdust powder and 10% H_2O_2 (5 g of cellulose for every 100 mL of H_2O_2). The pH of this mixture was fixed at 11.5 using NaOH, and it was stirred at 80°C for 30 min. Once the reaction was completed, the powder was separated from the solution by a filtering process. The obtained powder was rinsed until the pH returned to normal, followed by air drying for a period of 1-3 days.

2.3 Sawdust composite synthesis

A beaker containing 100 mL of distilled water was used to introduce magnetic nanoparticles (Fe_3O_4) at two different concentrations: 0.0wt% (control) and 10.0wt%. Subsequently, the mixture was sonicated at a frequency of 20 kHz for a duration of 30 min. To create a sawdust composite, 5 g of dried sawdust powder was combined with the magnetic nanoparticles. The mixture underwent stirring for 30 min, followed by another round of sonication at 20 kHz for 30 min to mitigate agglomeration. Finally, the sawdust composite was subjected to oven drying at 60°C for a 20 h.

2.4 Crystalline analysis

The crystalline parameter of sawdust was observed by X-ray Diffraction(XRD) (Pan-Analytical, USA), at a diffraction angle from 5° to 90°. Segal formula is used to calculate crystalline degree (CD) and crystalline index (CI)[19], as follows equation 1 and equation 2, respectively.

$$CD = \frac{I_{[002]}}{I_{[002]} + I_{[am]}} \times 100\% \quad (1)$$

$$CI = \frac{I_{[002]} - I_{[am]}}{I_{[002]}} \times 100\% \quad (2)$$

Where: $I_{[002]}$ is the intensity at 2θ of about 22.0° and $I_{[am]}$ is the lowest intensity at 2θ about 18°.

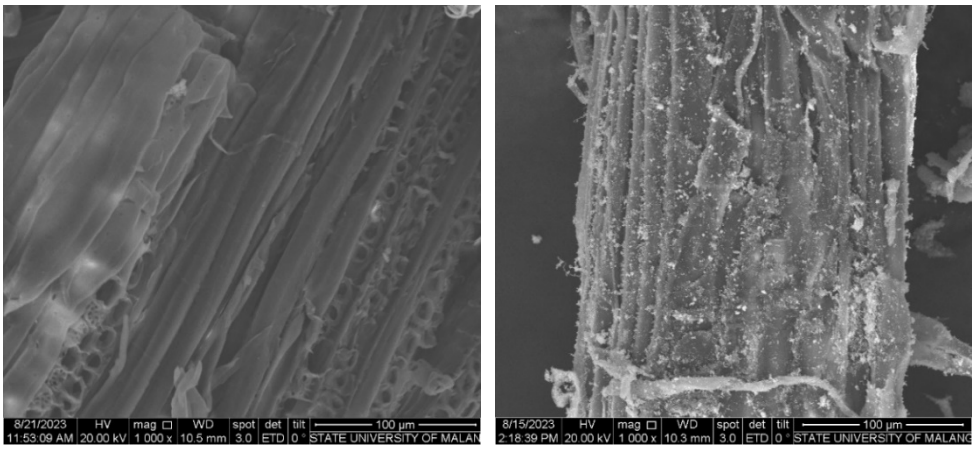
2.5 Morphology observation

The surface morphology of the sawdust nanocomposite was examined using an Electron Microscope (EM) (FEI Inspect-S50, Japan) operating at 25.000 V, following previous methods [20].

3 Results

3.1 Morphology analysis

Incorporating magnetic nanoparticles into sawdust powder changes the surface morphology of sawdust powder, as depicted in Figure 1.



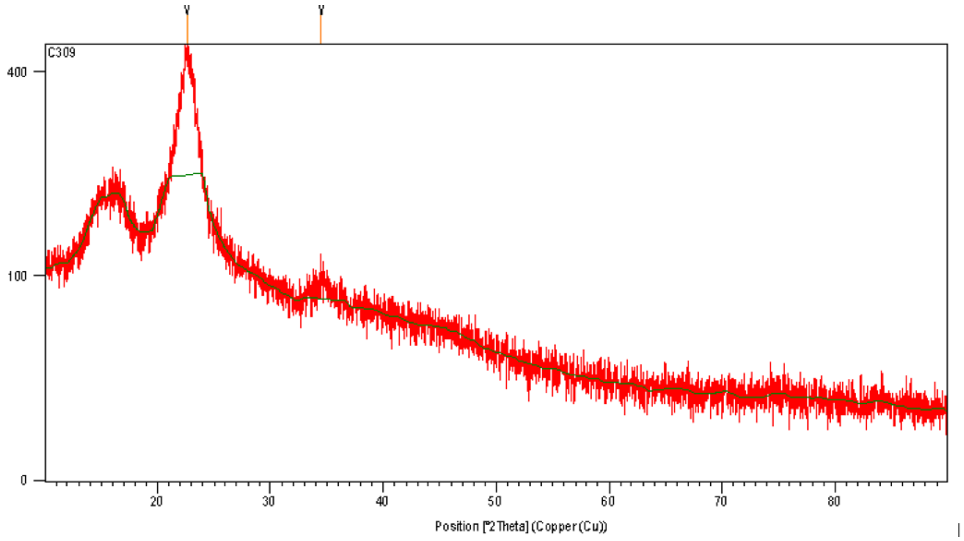
(A) (B)

Fig. 1. Surface morphology of sawdust powder (A) and sawdust with magnetic particles 10wt% (B).

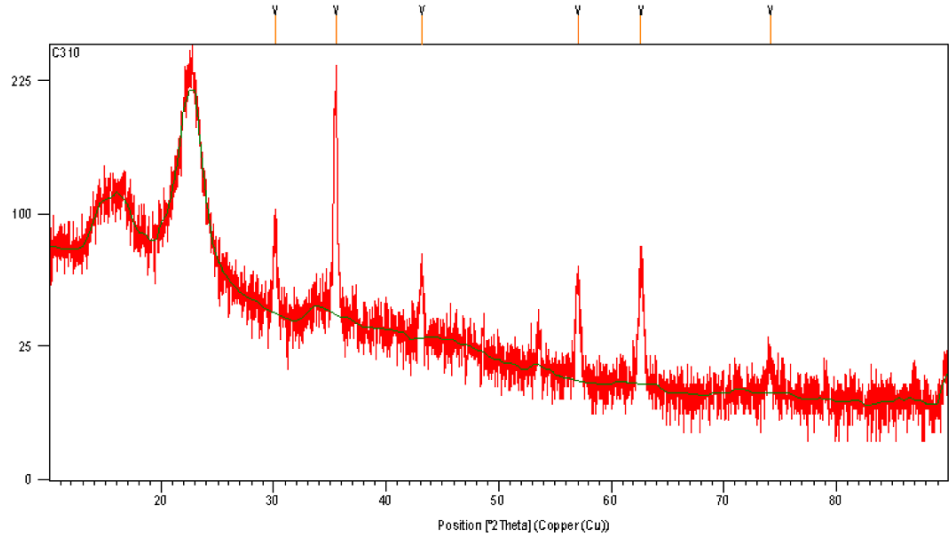
The structure of sawdust without magnetic nanoparticles shows the fiber walls and lumen (Figure 1A). Following the introduction of magnetic nanoparticles, surface of sawdust powder exhibits the presence of numerous deposited magnetic nanoparticles, as shown in Figure 1B. These magnetic nanoparticles tend to cluster on the surface, leading to a rougher texture. This phenomenon is a consequence of the inherent tendency of magnetic nanoparticles to adhere to adjacent particles forming agglomerate, a characteristic behavior of such nanoparticles [21]. Moreover, aside from adhering to the surface, the magnetic nanoparticles also become incorporated within the sawdust powder, leading to additional aggregation of these nanoparticles within the sawdust. Moreover, the magnetic nanoparticles exhibit a strong affinity for cellulose, primarily through hydrogen interactions. Nevertheless, a significant interaction between these magnetic nanoparticles and cellulose can have an impact on the overall structure of the sawdust powder.

3.2 Crystalline analysis

Figure 2 depicts the diffraction patterns of the sawdust powder composite. The diffractogram of the sawdust powder composite reveals four prominent peaks located at 15.1°, 16.5°, 22.8°, and 34.4°. These peaks correspond to the crystal planes of [110], [10], [200], and [004], respectively, indicating the presence of cellulose Iβ [21][22][23]. Additionally, the presence of magnetic particles is evident in the sawdust powder, as indicated by diffraction angles at 30.5°, 35.6°, 43.2°, 53.6°, 57.1°, 62.7°, 71.1°, 74.1°, and 86.8°. These detected peaks correspond to the crystal planes of [220], [311], [400], [422], [511], [440], [620], and [622] (JCPDS No. 19-0629). The magnetic particles in the sawdust powder are clearly visible in the accumulation on the surface of the sawdust particles.
The crystalline degree of sawdust powder is 76.1% and crystalline index of sawdust powder is 68.6%. Adding magnetic nanoparticles of 10.0 wt%, slightly reduces the crystalline degree of 75.70%, and also the crystalline index of 67.91%, respectively. The elevated concentration of nanoparticles disrupts the cellulose crystal network, resulting in a more randomized cellulose arrangement and a subsequent reduction in crystal value [23].



(A)



(B)

Fig. 2. Surface morphology of sawdust powder (A) and sawdust with magnetic particles 10wt% (B).

4 Conclusion

The addition of magnetic nanoparticles on sawdust powder was observed. The structure of the surface of the sawdust powder revealed that magnetic nanoparticles were distributed, deposited onto its surface, and formed clusters on the surface. Sawdust powder composite indicates some new peaks in the diffractogram due to adding magnetic nanoparticle. The introduction of magnetic nanoparticles led to a minor decrease in the composite material's crystalline properties, both in terms of degree and indexing

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