Synthesis and characterization of amine-functionalized sugarcane bagasse fiber magnetic nanoparticle biocomposites

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Synthesis and characterization of amine-functionalized sugarcane bagasse fiber magnetic nanoparticle biocomposites

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Abstract. Sugarcane bagasse is one of the by-products in the sugar industry which contains 60% of cellulose. Cellulose can be used as a matrix for biocomposite. The purpose of this research was to produce amine-functionalized sugarcane bagasse fiber magnetic nanoparticle biocomposites (SBB). The SBB was produced from sugarcane bagasse (SB) by solvothermal reaction. The SB was dried and blended into small size (±60 mesh), then lignin was removed with 1% NaOH (w/v) through the delignification. The biocomposites was made by adding delignified SB (SB-D) into a mixture of ethylene glycol, $FeCl_3.6H_2O$, and hexamethylenediamine (HMDA) in solution, and then heated for 6 h at 200 °C. HMDA as an amine source was applied different concentrations (5, 7, and 9 mL). The surface morphology of biocomposites was covered by the magnetic nanoparticles along SB-D which contained amine of about 17.78 mmol/g. The Fe content of SBB was 98.34% which had specific peaks for magnetite at 36°, 43°, and 57° which were measured by X-Ray Diffraction (XRD). The Fourier Transformed Infrared (FT-IR) identified N–H bending vibration on SBB at 1640 cm^{-1}. The iron content and amine group on the surface may affect high adsorption capacity for a wide range of biological pollutants.

1. Introduction

Sugarcane bagasse is a by-product of the extracting liquid sugar cane industry. A factory can produce sugarcane bagasse around 35-40% from the ground sugar cane weight. The sugarcane bagasse needs a further process to gain the added value. Based on a chemical analysis, sugarcane bagasse consists of lignin (22.09%), silicon dioxide (3.01%), cellulose (37.65%), pentose (27.97%), essence (1.81%), and ash (3.28%) [1, 2].

The researchers were interested to study about plant cellulose fibers because they are sustainable, natural, and environmentally friendly. Moreover, there are other advantages of using cellulose fibers such as easy to process, low cost, low energy consumption, lightweight, having excellent specific strength, harmless to the environment, and can be renewed and recycled compared to the conventional synthetic fibers [3]. Cellulose in sugarcane bagasse is coated by lignin which makes a strong structure. For further use as an adsorbent, lignin can disrupt cellulose to bind metal ions. Delignification is a process for the lignin removal. The delignification treatment used is a chemical treatment with NaOH solution. This solution can damage the structure of lignin, crystalline, amorphous parts, and cellulose bloating [4]. Meanwhile, biocomposite is a composite material consisting of natural polymers or bio-fibers (natural fibers) as a reinforcement that can be degraded.

Numerous investigations on the development of sugarcane bagasse have been reported, including the production of microcrystalline cellulose and nanocrystal [5], ethanol [2], biofuel [6] and resin [7].

Especially related to biocomposite materials, many researchers have paid their attention to use sugarcane bagasse as a matrix to form cardanol-formaldehyde composites [8], polyester matrix [9], and polyethylene matrix [10]. The utilization of sugarcane bagasse with magnetic nanoparticles is potential to be developed as biocomposites.

The solvothermal method through a one-step process of surface modification with an amine group has been carried out to synthesize the cellulose-based biocomposites with magnetic nanoparticles [11, 12]. However, there has been no research that develops the modified magnetic nanoparticles based on sugarcane bagasse fibers by a one-step process; thus, further optimization process is necessary to improve the surface functionalization and stability of biocomposites. This research focuses on using sugarcane bagasse fibers to be functionalized by an amine group on magnetic nanoparticle biocomposites. The present work investigates the magnetic nanoparticle biocomposites of sugarcane bagasse which is optimized on the amine content that made through a one-step process of solvothermal method. The surface morphology, iron content, crystalline structure, and functional group of biocomposites are also investigated.

2. *Materials and methods*

2.1. *Materials*

The sugarcane bagasse was obtained from an iced-sugarcane seller in Banjarbaru, South Kalimantan. Besides, iron trichloride hexahydrate ($FeCl_3.6H_2O$), ethylene glycol ($C_6H_6O_2$) sodium acetate anhydrous ($C_2H_3NaO_2$), hexamethylenediamine (HMDA), ethanol (C_2H_5OH), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Sigma Aldrich.

2.2. *Delignification of sugarcane bagasse*

Sugarcane bagasse (SB) was washed with distilled water and dried for 3 hours at 80 °C in an oven, mill-grinded to result in SB powder that could pass a 60-mesh sized sieve. The delignification process was carried out by adding the NaOH (1% w/v) solution and 4% w/v of SB powder into the flask and allowed for 2 hours at 80°C until the lignin was removed. The flask and its content were cooled to a room temperature for 2 hours. Then the samples were filtered by a filter paper. Distilled water was used to wash the samples until the pH of the filtrate became neutral. At last, the delignified fibers of SB (SB-D) were dried in an oven for 6 hours at 80°C.

2.3. *Synthesis of sugarcane bagasse fiber with magnetic nanoparticle biocomposites*

Solvothermal reaction is one of the methods for SB biocomposites with magnetic nanoparticle synthesis. Firstly, 1.6 g of sodium acetate anhydrous and 0.8 g of iron trichloride hexahydrate were dissolved in the sugarcane bagasse fibers (SBF) (0.5 g) in 24 mL of ethylene glycol by robust stirring at 50°C. The surface of amine-functionalized MNPs were synthesized by adapting the procedure by Wang, et al [13]. When hexamethylenediamine was added, the solution turned into dark orange. Next, the solvothermal was conducted for 6 hours at 200 °C then cooled at a room temperature. HMDA was added by 5, 7, and 9 mL. The SB biocomposites (SBB) were collected from the solution by employing an external magnet. Afterward, the SBB were rinsed with deionized water followed by ethanol three times for each. The SBB were kept in deionized water for the subsequent use. This synthesis produced 3 types of biocomposites: SBB-5, SBB-7, and SBB-9. SBB-5, SBB-7, SBB-9 got the addition of 5, 7, 9 mL of HMDA, respectively.

2.4. *Characterization*

The investigation of the structural morphology of SB, SBF, SBB-5, SBB-7, SBB-9 was conducted using Field-Emission Scanning Electron Microscopy (FE-SEM, JOEL JSM-6500 LV). XRF measurement was performed on Energy–disperse X-ray Fluorescence while the operation voltage and the current were kept at 20 kV and 77 uA. The surface functional groups on SB, SBF, SBB-5, SBB-7, and SBB-9 was identified by Fourier transform InfraRed spectrometry (Bio-rad, Digilab FTS-3500). Philips type X'Pert Scan Parameters by using Copper K-alpha (CuKα) radiation performed the X-

ray diffraction (XRD) measurement. The operation voltage and the current were kept at 40 kV and 30 mA, respectively. The crystalline index was calculated as equation 1.

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where CrI is Crystalline Index (%), I_{002} is intensity of crystal part and I_{am} is intensity of amorph.

2.5. Analysis

The retro-titration method was used to determine the amine content on the samples [14]. 50 mg of samples drop into 0.01 M HCl (25 mL). The mixture was shaken for 2 hours at a room temperature. After the centrifugation, the supernatant (5 mL) was titrated with 0.01 N NaOH. The amine concentration was calculated by equation 2.

$$C_{NH_2} = \left[\frac{(C_{HCl} \times V_{HCl}) - (5C_{NaOH} \times V_{NaOH})}{m_{sample}}\right] \quad (2)$$

where C_{HCl} is HCl concentration (mmol/L), C_{NaOH} is NaOH concentration (mmol/L), the volume of HCl is notated by V_{HCl} (L), the volume of NaOH is notated by V_{NaOH} which was used in the titration of excess non-reacted acid (L), and m is the sample mass (g).

3. Results and discussions

The lignin removal from the sugarcane bagasse was confirmed by the morphological structure and color. The original color of sugarcane fibers was cream and changed to darker (closer to grey) after the delignification process (figure 1). Based on the FE-SEM observation, SB looked slightly damaged due to the grinding process (figure 1a), but the lignin was still bound to cellulose and hemicellulose which were arranged in one direction so that the sugarcane fibers looked flat and intact. The contact area and porosity of the material could be increased by grinding. Meanwhile, the delignification process conduced the damage of SB-D from the surface to the inside. Consequently, the lignocellulose structure bonds began to open and the structure became irregular. Rodrigues, et al [7] observed unmodified sugarcane bagasse fibers which had large amount of extractives. After the delignification, the extractives on the surface of fibers were removed. Delignification with NaOH induced the decomposition of hemicellulose, lignin, and silica contained in the SB-D (figure 1b).

The delignification process reduced the size of fiber. The average diameter of bagasse fiber (25 µm) was lower in the raw bagasse. The fiber had smooth surface after the removal of lignin, hemicellulose and pectin [15]. XRF analysis showed a decrease of 31.5% silica in SB-D after treatment. Indeed, SB contained 31.5% Fe which then significantly increased up to 98.7% due to the formation of magnetic nanoparticles. The Fe content may affect the materials as an adsorbent by enhancing the high-adsorption of sorbent capacity for reactivity toward a wide range of biological pollutants [16].

The morphological structure of sugarcane bagasse fiber magnetic nanoparticle biocomposites with different concentrations of HMDA is shown in figure 2. The addition of 5, 7, and 9 mL of HMDA produced biocomposites with the same Fe content around 98.70%. The magnetic nanoparticles were formed on the fiber surface. Hexamethylenediamine played a key role in diminishing the magnetic size during its growth in the solvothermal reaction. The amine contents in biocomposites for the addition of 5, 7, and 9 mL HMDA were 3.21; 17.78; and 3.83 mmol/g, respectively. The different concentrations of amine could be analyzed by the morphological structure of biocomposites. The formation of magnetic nanoparticles for the addition of 5 and 9 of HMDA turned to aggregate and did not distribute on the fiber surface (Figure 2a and 2c). In comparison to 7 mL of HMDA, the magnetic more clearly distributed on the fiber surface (Figure 2b). This is why the amine contents on the surface of magnetic had different amounts. On other hand, the different concentrations of HMDA in this research did not have a big impact on the size of particles. The results obtained were in line with the previous research for magnetic formation by the solvothermal method [13, 17, 18].

XRD analysis was carried out to determine the cellulose crystal structure contained in the samples and the Crystalline Index (CrI) of sugarcane bagasse fibers before and after the delignification.

Cellulose crystals could be identified at an angle of 2θ between 20º-40º at which there were dominant peaks. Cellulose fiber was composed of several million microfibrils. These microfibrils fiber were divided into two different parts: the amorphous part formed from cellulose chains with crystalline and the flexible masses made of cellulose chains with strong bonds in a rigid linear arrangement. This crystal part was isolated to produce high-quality microcrystalline cellulose.

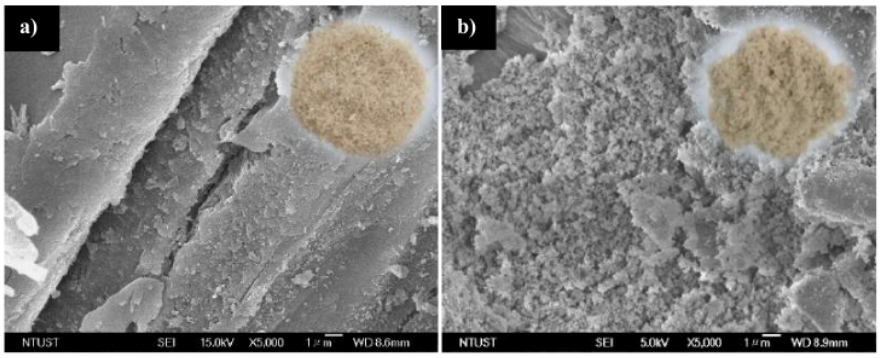

Figure 1. Images for FE-SEM of sugarcane bagasse fibers (a) before (SB) and (b) after delignification (SB-D).

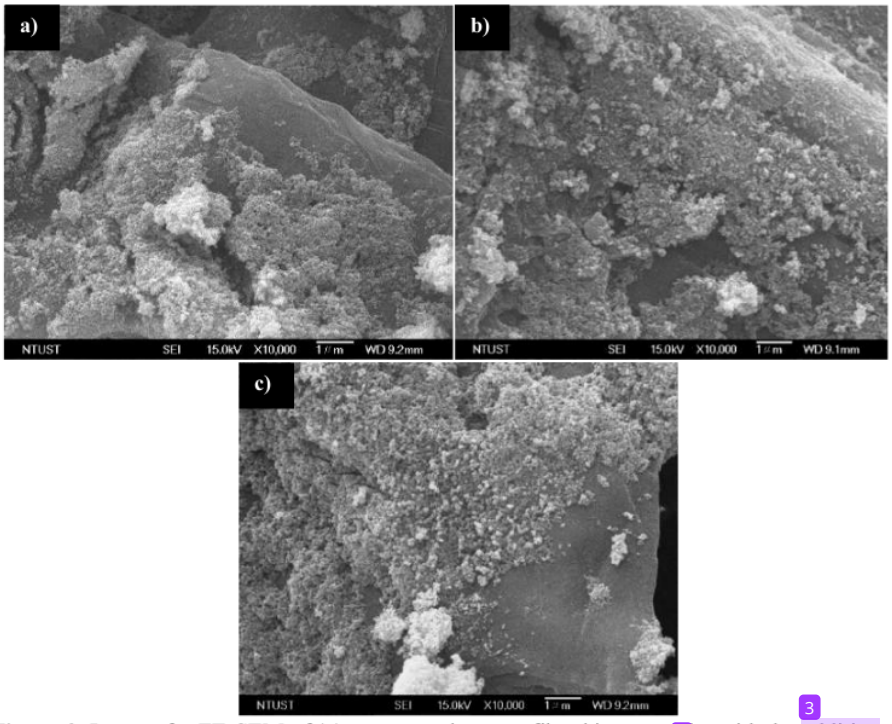

Figure 2. Images for FE-SEM of (a) sugarcane bagasse fiber biocomposite with the addition of 5 mL of HMDA (SBB-5) (b) sugarcane fiber biocomposite with the addition of 7 mL of HMDA (SBB-7) and (c) sugarcane fiber biocomposite with the addition of 9 mL of HMDA (SBB-9).

Table 1. Characterization of SB and SBF.

Sample	Characterization of Peak		CrI (%)
	Amorph (16.78°)	Crystal (21.69°)	
SB	567	782	37,9189
SB-D	683	1035	51,5373

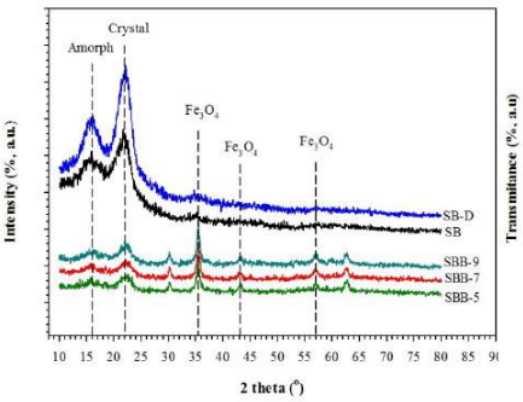

Figure 3. X-Ray Diffraction (XRD) pattern of materials: before (SB) and after delignification (SB-D) and sugarcane bagasse fiber biocomposites of SBB-5, SBB-7, and SBB-9.

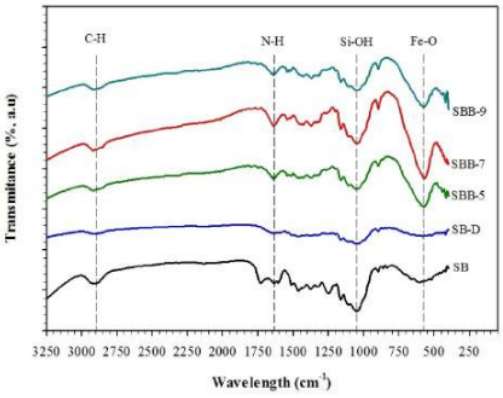

Figure 4. FT-IR spectrum of materials: before (SB) and after delignification (SB-D) and sugarcane bagasse fiber biocomposites of SBB-5, SBB-7, and SBB-9.

Cellulose was a parameter that determined the strength of the fibers, hence the product could be influenced by the crystal structure of cellulose. The sugarcane bagasse structure before and after the treatment still had components in amorph form (hemicellulose and lignin) and crystal (cellulose). The characterization of peaks for SB which contained cellulose fibers were identified at 2 tetha (°) = 16.78 in the amorphic form and 21.69 in the crystal form (figure 3). Table 1 shows the increase of SB-D CrI value after the delignification from 37.919% to 51.537% or an increase in crystallinity of 35.91%. This finding was similar to the sugarcane bagasse treatment by alkaline which had crystallinity index about 63.15% (15). It could also be proven from the peak intensity of SB-D which was sharper compared to SB. The treatment of SB with NaOH could change the structure of amorphous cellulose to crystalline cellulose due to the loss of hemicellulose and lignin content after the delignification.

XRD analysis was also used to identify the formation of magnetic nanoparticles in biocomposites, as it clearly appeared peaks at 36°, 43°, and 57°. These specific peaks were identified as magnetite (Fe_3O_4) which was appropriate for the crystalline magnetite standard pattern (JCPDS card 39-0664). figure 3 shows the different crystalline structures in the biocomposites compared to SB and SBF because of the existence of magnetic nanoparticles on SB-D surface. The peak for Fe_3O_4 particles was not found either in SB or SBF. In the case of different concentrations of 5, 7, and 9 mL of HMDA, all biocomposites had the same peak position due to the formation of Fe_3O_4. In addition, SBB-7 had the highest intensity at 36° probably because of the distribution of magnetic nanoparticles on the surface of SBF. This was also confirmed by the FE-SEM images for all biocomposites.

FT-IR spectrum of SB, SB-D, SBB-5, SBB-7, and SBB-9 are shown in figure 4. This analysis was used to detect the functional groups contained in the samples. C-H stretching vibrations as the bonds in SB and SB-D were detected at peak 2900 cm^{-1}. The peak at 1640 cm^{-1} for N-H bending vibration detected the modification of the amine group on the biocomposites. Based on the calculation of amine

group, the highest number of amine was on SBB-7 which was also proved by higher intensity peaks on N-H binding compared to the others. The peak at 580 cm^{-1} showed Fe-O stretching band component in Fe_3O_4. This peak was not detected on SB and SB-D because there were no magnetic components. The wavenumber at 1050 cm^{-1} corresponded to Si-OH and O-H band and could be read in all samples, which were also confirmed in the XRF analysis. The peaks at 1525 cm^{-1} and 1260 cm^{-1} in SB showed the aromatic C=C bond of lignin. In SB-D, SBB-5, SBB-7 and SBB-9, the peaks at 1525 cm^{-1} and 1260 cm^{-1} did not exist. This indicated that the lignin content was reduced and the cellulose was separated [15].

4. Conclusions

The synthesis of amine-functionalized sugarcane bagasse fiber magnetic nanoparticle biocomposites was successfully prepared by the solvothermal reaction. The addition of 7 mL of hexamethylenediamine was the best condition to achieve a higher amine content of about 17.78 mmol/g. The amine magnetic nanoparticles consisted of 98.34% Fe and the specific peaks for magnetite were at 36°, 43°, and 57°, measured by X-Ray Diffraction (XRD). The XRD analysis showed the delignification increased the crystalline index (CrI) of BSF up to 51.53%. In addition, the Fourier Transformed Infrared (FT-IR) identified N–H bending vibration on BSB at 1640 cm^{-1}. Due to sustainable, natural and easy process as well as low cost, and low energy consumption of sugarcane bagasse as raw material, it becomes a potential candidate to develop as an adsorbent for high adsorption capacity for a wide range of organic pollutants.

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