Preparation of magnetic nanoparticle biocomposites using rice husk and sugarcane bagasse fibers as the matrix

by Hesti Wijayanti

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Abstract. Fiber is one of the important components to construct a matrix structure. Biomass is a potential material as a fiber resource for matrix. Rice husk and sugarcane bagasse consist of 36.6 % and 60% cellulose, respectively. This current research focused on evaluating the production of amine functionalized magnetic nanoparticle biocomposites produced by mixture of rice husk (RH) and sugarcane bagasse (SB) fibers. First, RH and SB fibers were dried and crushed close to 60 mesh for each, followed by a delignification at 80 °C for 2 h in 1% w/v of NaOH. Through by one-step solvothermal process, it was done by adding delignified ratio of RH and SB fibers (1:1; 1:2; 1:3; 1:4) to mixture of ethylene glycol, $FeCl_3.6H_2O$, and 1.6-hexanediamine at 200 °C for 6 h. The magnetic nanoparticles appeared on the fibers surface which contained 97.97% Fe. The magnetite was formed proved by the specific peaks at 36°, 43°, and 57° by X-Ray Diffraction.(XRD). The Fourier Transformed Infrared (FT-IR) identified N–H bending vibration and Fe-O in the biocomposites at 1640 cm^{-1} and 582 cm^{-1}, respectively. The restructure of matrix, iron, and amine groups on the biocomposites surface can affect the adsorption capacity of various waste water treatments.

1. Introduction

One of the biggest natural resources in South Kalimantan is rice. South Kalimantan has a unique type of rice known as "*Beras Banjar*". Cellulose content in the rice husk is 34.34%–43.80% [1]. Besides rice husk, another organic material that contains fiber is sugarcane bagasse. Sugarcane has cellulose content about 35.3%-45.5% [2]. The utilization of rice and sugarcane bagasse will generate waste. A large amount of this waste has impacted the environment. Nowadays, rice husks are only used to compress soft or burn soil. As a result, the combustion activity can cause air pollution. Meanwhile, sugarcane bagasse is usually used for paper making, animal feed [3] or fuel in the inseminator. The fiber content in both materials has the potential to be natural fibers used in biocomposites material production. One of the utilization of biomass waste for various applications is the use of adsorbent as it has good specific strength and is lightweight, environmentally friendly, and easy to get due to its abundant availability in the nature [4].

Through this biomass waste technology approach, it can be isolated to obtain fiber or cellulose. The RH and SB were designed to be a matrix for the adsorbent in ion removal and as hybrid composites. Modification surface of rice husk and sugarcane bagasse fibers was done to increase the properties by chemical treatment technique [5]. Besides, de-polymerizing lignin, hydrolyzing hemicellulose and breaking the covalent bonds between lignocellulosic components were done using aqueous sodium hydroxide (NaOH) solution in the RH and SB fiber treatments [6]. Many researchers have reported

that utilization of biomass fibers is in accordance with the function as well as physical and mechanical properties of the material, such as an adsorbent that can absorb dyes [7,8] metal ions Cu (II) and Cd (II) and choromium [9,10] Pb(II) ions [11,12] and Fe(III) ions [13]. The combination of sugarcane bagasse fiber with carbon as an adsorbent as a biocomposite material to absorb color gives good results [14].

The source of fiber material in the composite manufacturing uses the cellulose fibers of RH and SB. The magnetic nanoparticles are attached on the fiber surface of RH and SB in the form of biocomposites by the matrix provided. In addition, the development of magnetic nanoparticle synthesis with a one-step process by modifying functional groups with rice husk fiber as an adsorbent has been investigated [1]. The novelty in this research is the fiber source for the biocomposites is from the combination of rice husk fiber and sugarcane bagasse fiber. There has been no research that develops biocomposites with a variety of these two fiber source compositions through a one-step process. This research is to investigate the best composition of combination of RH and SB fibers for the biocomposites formation. The characterization of biocomposites such as surface morphology, component content, crystalline structure, and functional groups are also investigated.

2. Materials and methods

2.1 Materials

The following are some materials used in this research. The rice husk was obtained in Gambut, Banjar District, and the sugarcane bagasse was obtained from an iced sugarcane seller in Banjarbaru South Kalimantan. There were also 1.6-hexanediamine ($C_6H_{12}N_2$), ethylene.glycol. ($C_6H_6O_2$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), sodium acetate anhydrous ($C_2H_3NaO_2$), ethanol (C_2H_5OH) that were taken from UPT BPPTK LIPI. Last, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Sigma Aldrich.

2.2. Delignification

Rice husk (RH) and sugarcane bagasse (SB) were washed to remove impurity particles, dried at 80 °C for 24 h then crushed using a blender, and the RH and SB powder was sieved to pass ± 60 mesh size. Afterward, the dry powder of RH and SB was dissolved in 1% NaOH solution (40% v / v) then stirred at 100 rpm for 2 hours and heated at 80 °C to remove the lignin. The RH and SB fiber powder was later washed with distilled water until the filtrate reached a neutral pH and dried for 3 hours at 80 °C. The results of fibers were in the forms of RH-D and SB-D.

2.3. Preparation of RH and SB fibers with magnetic nanoparticle biocomposites

The one-step solvothermal process was done to synthesize the combined fibers of RH and SB biocomposites that produced the magnetic nanoparticle biocomposites. First, 24 mL of ethylene glycol was added to 1.6 g of sodium acetate anhydrous and 0.8 g of iron (III) chloride were heated at 60 °C and stirred at 200 rpm for 15 minutes. During the time, 7 mL of 1.6 hexanediamine and 0.5 g of RH-D and SB-D were added into the solution with the weight ratios of 1:1; 1:2; 1:3 and 1:4. The mixture of fibers was put into a solvothermal reactor (Teflon Stainless Steel Autoclave) then heated at 200 °C for 6 h. After the reaction, the biocomposites were washed with distilled water and ethanol three times for each to remove any residual chemicals. Finally, it produced four types of biocomposites, namely BM-1:1, BM-1:2, BM-1:3; and BM-1:4.

2.4. Characterization

Analysis of Field-Emission Scanning Electron Microscopy (FE-SEM, JOEL JSM-6500F) was used to observe the morphological structure of RH, BS, RH-D, SB-D, and BM. XRF measured the energy-dispersive X-Ray Fluorescence with a condition operation at 20 kv voltage and 77 UA current. The functional groups of the surface on RH, RH-D, SB, SB-D and BM were identified by Fourier Transform Infra-Red Spectrometry (FT-IR, bio-rad, digilab FTS-3500). Measurement of the X-ray

Diffraction (XRD) by using copper k-alpha (CuKα) radiation was performed using the Rigaku D/max-b XRD. The condition was kept at 400 kv voltage and 100 ma current. Crystalline Index (CrI) was calculated as in equations 1.

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

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

2.5. Analysis

Retro-titration method was conducted to determine the amine contents in the samples [15]. In brief, the analysis started by dropping 50 mg of samples into 0.01 M HCl of 25 mL. The mixture was shaken for 2 hours. Then, 5 mL of supernatant was titrated with 0.01 N NaOH after the centrifugation. The concentration of amine was calculated as in equations 2.

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

where m is mass of sample (g), C_{NaOH} is concentration of NaOH (mmol/L), V_{NaOH} is volume of NaOH which used in titration of unreacted acid excess (L), C_{HCl} is HCl concentration solution (mmol/L) and V_{HCl} is volume of HCl (L)

3. Results and discussion

Rice husk (RH) and sugarcane bagasse (SB) are biomass cellulose that have a complex structure. In order to collect the cellulose, the materials should be processed through delignification. RH and SB gave differences on the structures of morphology and crystal, and functional groups in the samples. After the delignification process, the color of rice husk fiber changed from the initial color brown to grey. On the other hand, the original color of SB before the treatment with NaOH solution was brown and became brighter after the treatment. The changing of color in the materials is shown in figure 1 and 2 (inset). The micrograph results of rice husk and sugarcane bagasse in 60-mesh size by FE-SEM analysis with 5000x magnification are also shown in figure 1 and figure 2. Based on figure 1a, the surface of rice husk formed a lump which was identified as silica concentrated at a certain point observed by FE-SEM. Meanwhile, the surface of sugarcane bagasse fiber (figure 2a) had the conical protrusions and bright spots at the in-order distance identified as silica which was concentrated in the domical protrusion area, so that the fiber surface looked very undulated and had side-by-side sloping areas [16].

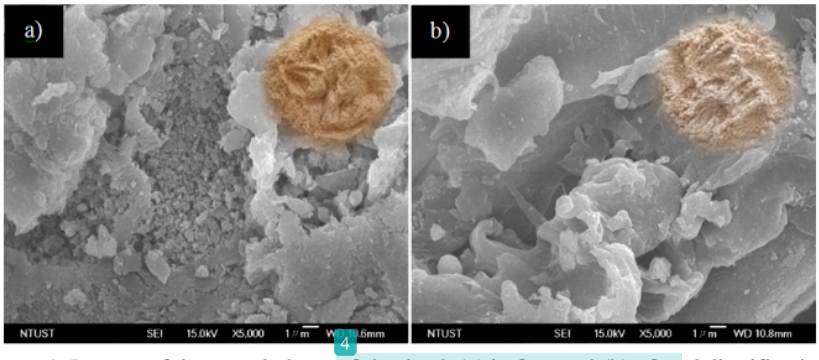

Figure 1. Images of the morphology of rice husk (a) before and (b) after delignification.

Rice husk and sugarcane bagasse fibers were produced through the delignification process by decomposing lignin, hemicellulose and silica contained in the fibers. In this case, the increasing roughness of the surface and the cracking of conical protrusions occurred due to the treatment with NaOH solution. In addition, due to the leaching of lignin, hemicellulose and silica the RH-D and SB-D became shrinking as shown in figure 1b and figure 2b.

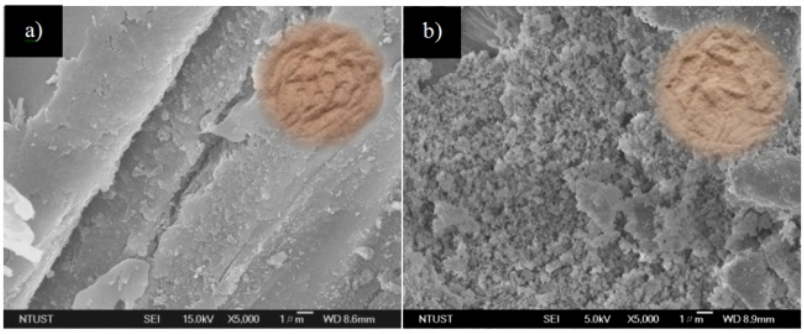

Figure 2. Images of the morphology of sugarcane bagasse (a) before and (b) after delignification.

The morphological structure of magnetic nanoparticle biocomposites with the addition of 1.6-hexanediamine is shown on figure 3. The magnetic nanoparticles were grown on the fiber surface and smaller in size around 30-50 nm. To determine the particle size and to modify the surface spontaneously, hexanediamine played an essential role in the process of magnetic formation. The 1.6-hexanediamnie in the mixture will inhibit the magnetic growth from $FeCl_3$ because the amine groups are kept on the surface that prevents the particle growth [17]. The results of this study regarding the formation of magnetite are in accordance with the findings from [1,18,17].

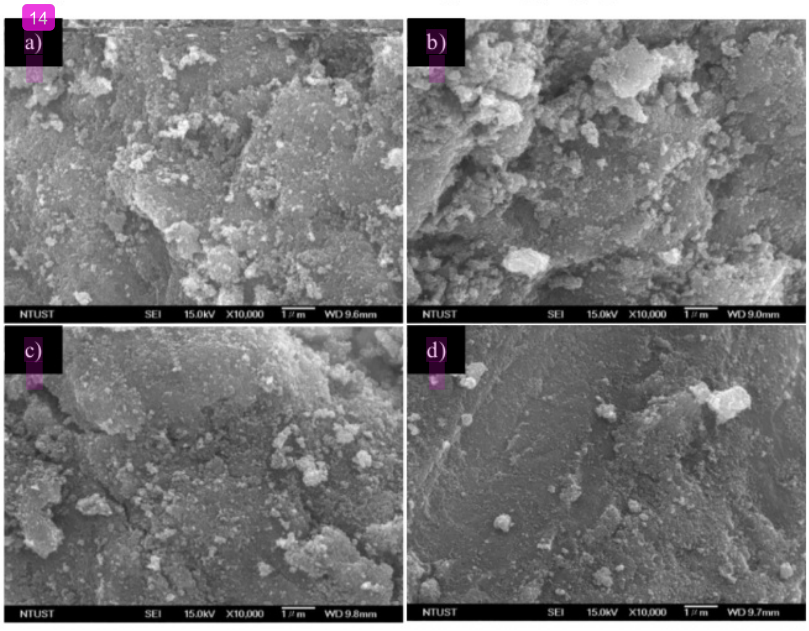

Figure 3. Images of the morphology of rice husk and sugarcane bagasse biocomposites of a) BM-1:1; (b) BM-1:2; (c) BM- 1:3 and (d) BM- 1:4.

A different ratio of RH-D and SB-D in the preparation of biocomposites has shown a number of magnetic that could be produced from these materials. As shown in figure 3, all samples had been distributed well on the surface of fibers. Due to the structure and composition of the fibers, the samples had slightly different amine contents. The BM-1:1, BM-1:2; BM-1:3; and BM-1:4 contained as much as 2.64; 2.30; 2.30; 2.37 mmol/g of amine group, respectively. Further, the iron contents of BM-1:1, BM-1:2; BM-1:3; and BM-1:4 were detected by XRF as much as 97.97%, 97.52%, 96.49% and 95.58%, respectively. As a result, the highest iron and amine contents were found in the biocomposisites with ratio 1:1 or BM-1:1.

Analyses for crystalline index (CrI) and cellulose crystal structure of rice husk (RH) and sugarcane bagasse (SB) were done through XRD. The cellulose crystal displayed dominant peaks shown at an angle of 2 theta between 20°-80° [19]. In order to calculate the intensity of crystal in the samples, it was taken between the angles by XRD data. Meanwhile, the amorph characteristic showed wide diffraction of angle XRD pattern at 2 angle between 0°-20° at which the XRD pattern was seen to diffract widely [20]. Additionally, the lignocelluloses which contained cellulose had peaks in its amorphous form at 16.0° (cellulose I) and at 22.2° (cellulose II) in its crystal form (figure 4). The delignification treatment with NaOH solution of rice husk (RH) and sugarcane bagasse (SB) fibers could increase the intensity or crystal structure of the rice husk (19) and sugarcane bagasse fibers This caused the loss of hemicellulose and lignin content after treatment.

This study also recorded the increased crystalinity index (CrI) values of rice husk and sugarcane bagasse fibers which were 90.32% and 36.8% respectively as displayed in table 1. The crystalline cellulose had been formed due to the increased intensity of the crystal peaks while the peak of amorph showed a reduced polysaccharide structure identified through a broad peak [21]. The crystalline and amorph peaks were used as the indication to measure the organized crystalline cellulose and a less-organized polysaccharide structure.

Table 1. Components of peaks characteristics of RH, RH-D, SB, SB-D.

Samples	Characteristics of Peaks		CrI (%)
	Amorph (16.0 °C)	Crystal (22.2 °C)	
RH	464	665	43.319
RH-D	564	1029	82.447
SB	771	1208	56.680
SB-D	686	1218	77.551

The apparent magnetic on the samples also could be identified by XRD. Based on figure 4, the specific peaks for magnetite was at 36°, 43°, and 57° (JCPDS card 39-0664). This proved that the magnetic was successfully formed in the biocomposites. Based on research of Nata et.al., 2018 (1), the results showed that the formation of magnetite was 30-50 nm size, the iron content in RHB-MH was about 19.85% which confirmed by an EDX analysis and the increased crystalinity index (CrI) of rice husk was about 16.77% confirmed by XRD.

The results of FT-IR spectra of RH, RH-D, SB, SB-D, BM-1:1; BM-1:2; BM-1:3; BM-1:4 can be seen in figure 5. The vibration spectra at 582 cm^{-1} showed that Fe-O in Fe_3O_4 stretched for all the samples of biocomposites. This peak did not appear on the RH and SB fibers. Modification of amine group in the biocomposites for N-H bending vibration was also confirmed by the specific peak at 1640 cm^{-1}. In addition, the wavenumbers of RH and RH-D for C-H stretching vibration are shown at the peak of 2920 cm^{-1}. Last, the wavenumber of Si content in the fibers was detected at 1050 cm^{-1} as Si-OH band.

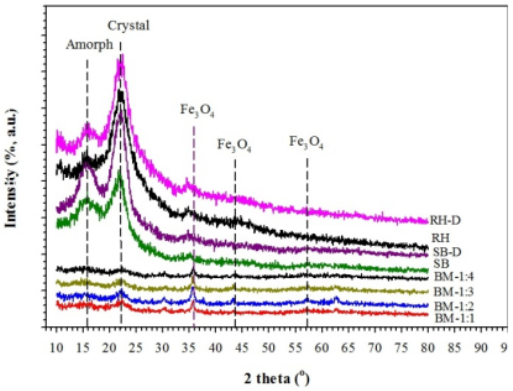

Figure 4. XRD analysis of RH, RH-D, SB, SS-D, BM-1:1; BM-1:2; BM-1:3; BM-1:4.

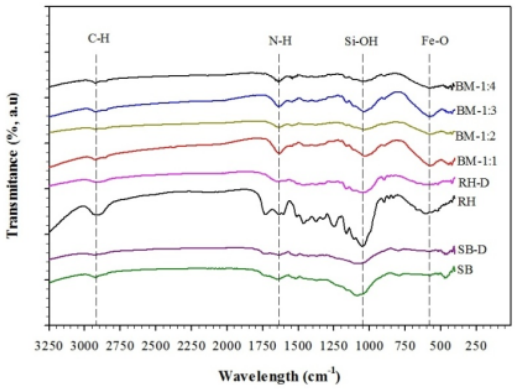

Figure 5. FT-IR spectra of RH, RH-D, SB, SS-D, BM-1:1; BM-1:2; BM-1:3; BM-1:4.

4. Conclusions

Some conclusions are drawn from this study. The combination of rice husk (RH) and sugarcane bagasse (SB) fibers as the matrix for biocomposites was successfully prepared by a one-step hydrothermal process. The magnetic nanoparticles were formed on the surface of rice husk (RH) and sugarcane bagasse (SB) fibers approved by XRD and FE-SEM analyses. The best composition of RH-D and SB-D fibers was achieved in a ratio of 1:1. Moreover, the amine content in the particle was about 2.6 mmol/g which was confirmed by FT-IR. The magnetite was formed in this reaction, and this was proved by the specific peaks at 36°, 43°, and 57° by XRD. The magnetic nanoparticles appeared on the fiber surface that contained 97.97% Fe. All in all, the magnetic nanoparticle biocomposites based on the cellulose is a potential candidate as a matrix for biocomposites.

Acknowledgements

We would like to express our thanks to the DGHE, Ministry of Education and Culture of the Republic of Indonesia for the financial support for magister thesis research with contract No. 113.1.12/UN8.2/PG/2020.

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