Rice Husk Fiber Magnetic Nanoparticle Biocomposites: Preparation and Characterization

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Abstract. The synthesis of biocomposites from rice husk (RH) fiber and magnetic nanoparticle was made by solvothermal reaction. Rice husk dried was blended to small size (60 mesh), then through delignification process to eliminate lignin by 1% w/v NaOH solution. Delignified rice husk was put into hydrothermal reactor, afterward was carried out by one-pot solvothermal at 200 °C for 6 h in the presence of 1,6-hexanediamine, FeCl₃·6H₂O and ethylene glycol. The process was produced two types of biocomposites, without amino group (RHB-M) and with amino group (RHB-MH). The characterization results shown by FE-SEM, magnetic nanoparticle have been formed on the surface of RH fiber with diameter size around 30–50 nm could be obtained. X-Ray Diffraction (XRD) analysis showed treatment of ED delignification was increased crystallinity index (CrI) about 16.77% and reduced silica content about 78%. The iron content may affect the adsorbent by enhancing the high-adsorption of sorbent capacity for reactivity toward a wide range of organic pollutant.

Keywords: biocomposite; rice husk fiber; magnetic nanoparticle; solvothermal

1. Introduction

Rice husk (RH) is by-product of the rice milling process and it is major waste product of the agricultural industry. It is reported that rice production in South Kalimantan increases annually about 8.3% every year. For every one million tons of paddy rice harvested, about 200 thousand tons of the RH is estimated to be burned, used as animal bedding or left in the field after harvest. In this case, the utilization of RH can disrupt environment and affect human health. In nature, rice husk is tough, insoluble in water, woody, has chemical stability, high mechanical strength and has silica–cellulose structural arrangement. It mainly consists of cellulose (32%), hemicelluloses (21%), lignin (21%), silica (20%) and crude protein (3%).

Through a technological approach, RH can be further processed into useful product. The utilization of RH was investigated to be concrete block, as a matrix for hybrid composites and as adsorbent for ion removal. Alkali treatment is a chemical treatment technique for surface modification of rice husk for the purpose of improving the properties. Treatment of rice husk with aqueous sodium hydroxide (NaOH) solutions breaks the covalent association between lignocelluloses components, hydrolyzing hemicelluloses and de-polymerizing lignin. The cellulose fiber of RH can be used as a source of fiber material in composite manufacture. The researcher were investigated the utilization of RH for nano-crystalline silica and carbon composites, geopolymer composite, cellulose fiber and nanocrystal, and rice husk-blended polypropylene eco-composite. Furthermore, there is limited research which focuses on utilization of rice husk fiber (RHF) and magnetic nanoparticles (MNP) composites. It is interesting to find out the synergic effect of cellulose fiber and MNP material become bicomposites. In the form of biocomposites, the RHF provides template for MNP growth on the surface or along the fiber. In this research, the preparation and characterization of RH biocomposites with MNP were investigated and reported.
2. Materials and Method

2.1. Materials

Rice husk was obtained from rice mill at Martapura, South Kalimantan, ethylene glycol (C$_6$H$_6$O$_2$), sodium acetate anhydride (C$_2$H$_3$NaO$_2$), iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O), 1,6-hexanediamine (HMDA), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (C$_2$H$_5$OH) which have purchased from Sigma Aldrich without further purification.

2.2. Delignification of rice husk

Rice husk was washed with distilled water and dried at 80 °C for 3 h in an oven, mill-grinded and the RH powder could pass through 60 μm mesh. The powder of RH (45% w/v) was followed delignification process by adding 1% w/v of NaOH solution into the flask and allowed at 80 °C for 2 h for eliminate the lignin. After 2 h, flask and its content was cooled to ambient temperature. Sample were filtered in a Buchner funnel and washed by hot distilled water until the pH of filtrate become neutral. Finally, the delignified fibers of RH (RHF) were dried on oven at 80 °C for 6 h.

2.3. Preparation of rice husk fiber with magnetic nanoparticles biocomposites

The synthesis of RH biocomposites with MNPs was carried out by one-pot solvothermal reaction. Briefly, anhydrous sodium acetate (1.6 g) and FeCl$_3$·6H$_2$O (0.8 g) were dissolved in ethylene glycol (24 mL) with vigorous stirring at 50 °C in the presence of 0.5 g of RHF. Surface amine-functionalized MNPs were synthesized adapting to the procedure used by Wang et al., 2006 [11]. When 1,6-hexanediamine (HMDA) (7 mL) was added, the solution turned into dark-orange, then solvothermal was conducted at 200 °C for 6 h.

After cooling to room temperature, the RH biocomposites were collected from the solution by employing external magnet and was rinsed with deionized (DI) water followed by ethanol each for 3 times. The obtained RH biocomposites with MNPs were kept in DI water for future use. There are two types of RHF biocomposites production, added and without the addition of HMDA. The biocomposites product was without the amino group (RHB-M) and with the amino group (RHB-MH).

2.4. Characterization of RHB-M and RHB-MH

The investigation of structure morphology of RH, RHF, RHB-M, and RHB-MH were used Field-Emission Scanning Electron Microscopy (FE-SEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDAX). The X-ray diffraction (XRD) measurement was performed on Rigaku nD/MAX-B X-ray diffractometer by using Copper K-alpha (CuKα) radiation. The operation voltage and current were kept at 40 kV and 100 mA, respectively. Fourier Transform Infra Red spectrometry (Bio-rad, Digilab FTS-3500) was used for identified the surface functional groups on the RH, RHF, RHB-M and RHB-MH.

3. Result and Discussion

The rice husk before and after NaOH treatment was gave difference on the rice husk morphology, structure and surface functionalization during treatment. The original color of RH before treatment shows brown powder (Fig. 1a) and after treatment the colour become lighter (Fig 1b).
Figure 1. Photograph of rice husk (a) before treatment and (b) after treatment

The FE-SEM micrographs of rice husk (a) and RHF (b) are showed in Fig. 2. As seen in Fig. 2(a), the surface appeared highly undulated due to the presence of regularly spaced conical protrusions and bright spots which can be attributed to silica which is more highly concentrated in regions corresponding to dome shaped protrusions and adjoining sloping areas [2]. Treatment with NaOH induced the cracking of the conical protrusions, and increased the surface roughness. The surface also showed higher roughness and cracks in the direction of the major axis of rice husk. This could be a consequence of the preferential elimination of the cementing materials of the interfibrillar region (mainly hemicelluloses and lignin). After treatment, the RHF become shrinking about 74% in wide due to leaching of silica, hemicelluloses and lignin.

Figure 2. FE-SEM image of rice husk (a) before treatment and (b) after treatment

Fig. 3 shown the surface texture of RHF biocomposites material by added and without the addition of amino group using HMDA. Base on the photograph, monodispersed nanoparticles were aggregated, which was due to the nanosize of Fe$_3$O$_4$ on the surface of fiber. Surface of RHB-M and RHB-MH are attached by MNPs. In comparison with RHB-MH prepared under the same conditions using HMDA (Fig. 3b), the size of MNPs formed on are much smaller, nearly monodispersed with a diameter of about 30 nm which agrees well with that observed by previous investigators [11-13]. Evidently, HMDA plays the key role in reducing the size of MNPs during its growth in the solvothermal reaction. Presumably, the amino group on the terminal of HMDA participates in the formation of Fe$_3$O$_4$ from FeCl$_3$. Once grafted onto the surface of MNPs, HMDA will prevent the further growth of MNPs because it blocks the transport of ferric ions to the nucleation site on MNPs [12].
The MNPs growth in situ of the RHF was also confirmed by EDX analysis, which proved that iron contains of RHB-M and RHB-MH about 14.33% and 19.85%, respectively. The EDX result is shown in Table 1. In addition, the concentration of silica also reduced 78% after treatment by NaOH.

Table 1. EDX component of RH, RHF, RHB-M and RHB-MH

| Component | Concentration (% weight) |
|-----------|--------------------------|
|           | RH | RHF | RHB-M | RHB-MH |
| C         | 23.78 | 48.27 | 40.03 | 30.14 |
| O         | 46.93 | 45.96 | 41.45 | 45.31 |
| Si        | 29.29 | 5.77  | 4.18  | 4.70  |
| Fe        | -   | -   | 14.33 | 19.85 |

Fig. 4 shows the X-ray diffraction analysis of RH, RHF, RHB-M, and RHB-MH. The typical spectrum of cellulosic crystalline material, having amorph peak at 2θ = 16.2 and crystalline peak at 2θ = 22.6. The X-ray diffractograms show an increase in the degree of crystallinity of RH from 27% to 44% after treatment with NaOH, as evident from the sharper diffraction peak RHF compared to that of RH. This is due to the fact that NaOH removes natural fats, waxes, silica, lignin and hemicelluloses from the RH surface. The main crystalline peak is taken as indicative of highly organized crystalline cellulose, while the amorph peak is a measure of a less organized polysaccharide structure and assigned to broad peak with low angle [14]. In the case of diffraction peaks of RHB-MH, was changed the crystalline structure, because of presence MNPs on the surface of rice husk fiber.

The formation of the magnetite can also be seen in the XRD peaks of Fe$_3$O$_4$ around at 36. This line is characteristic for spinel Fe$_3$O$_4$. Magnetic nanoparticles are close to the standard pattern for crystalline magnetite (JCPDS card 39-0664).
Figure 4. XRD analysis of RH, RHF, RHB-M, and RHB-MH

FT-IR spectra of RH and RHF are shown in Fig. 5. The C-H stretching vibration of the RH and modified RHF are manifested through a strong peak at 2930 cm$^{-1}$. From the infrared spectra shown in this figure, the absorption peaks at 580 cm$^{-1}$ belonged to the stretching vibration mode of Fe-O bonds in Fe$_3$O$_4$, even for EDB-M and EDB-MH, while at this peaks the stretching vibration did not appear for RH and RHF, respectively. The present of amine group on RHB-MH is accordant with that of the band around 1540 cm$^{-1}$ was due to the N–H bending vibration. The iron content may affect the adsorbent by enhancing the high-adsorption of sorbent capacity for reactivity toward a wide range of organic pollutants [15].

Figure 5. FT-IR Spectra of RH, RHF, RHB-M, and RHB-MH

4. Conclusion

The rice husk fiber and magnetic nanoparticle biocomposites was successfully prepared by one step hydrothermal treatment. The characterization results shown by FE-SEM, magnetic nanoparticles have been formed on the surface of rice husk fiber. Amine functionalized on biocomposites has effects to diameter size of magnetite nanoparticle about 30-50 nm. Rice husk fiber is a promising candidate to be used as template for biocomposite. X-Ray Diffraction (XRD) analysis
showed treatment of rice husk was increased the crystalinity Index (CrI) about 16.77% and reduced silica content about 78%.

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