Superabsorbent nanocomposite synthesis of cellulose from rice husk grafted poly(acrylate acid-co-acrylamide)/bentonite

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Abstract. Superabsorbent nanocomposite synthesis of cellulose rice husk as the backbone with free radical polymerization method in copolymerization grafted with acrylic acid and acrylamide monomer. The cellulose was isolated from rice husk with mixture of toluene and ethanol and then hemicellulose and lignin were removed by using potassium hydroxide 4% and hydrogen peroxide 2%. The obtained cellulose rendement was 37.85%. The functional group of lignin analyzed by FTIR spectra was disappeared at wavenumber 1724 cm\(^{-1}\). Crystal size of the obtained isolated cellulose analyzed by XRD diffraction pattern was 34.6 nm, indicated the nanocrystal structure. Copolymerization was performed at temperature of 70°C with flow nitrogen gas. Initiator and crosslinking agent used were potassium persulfate and N’N-methylene-bis-acrylamide. The swelling capacity of water and urea showed the results was quite satisfactory, the maximum swelling capacity in urea and water were 611.700 g/g and 451.303 g/g, respectively, and can be applied in agriculture to absorb water and urea fertilizer.

Keywords: rice husk, nanocomposite, cellulose, swelling capacity

1. Introduction
Rice husk is an agricultural by products that is biodegradable with three main components, namely cellulose, hemicellulose and lignin [1, 2]. Cellulose is natural polymer that has biodegradable, non-toxic properties, and abundant amounts in nature [3]. Cellulose can be converted to nanocellulose that would be outstanding if combined with inorganic nanoparticles, in order to obtain nanocomposites that have properties of both nanocellulose and nanoparticles [4]. Nanocomposite can be considered as solid structures in nanometer scale dimensions, repeated on the distance between the different forms of constituent structure [5]. Compared with the ordinary cellulose, nanocellulose has a smaller diameter <100 nm which makes nanocellulose has many unique properties, such as high mechanical strength and large surface area [6].

In this study, nanocellulose was used as the backbone to form a superabsorbent nanocomposite which will be used to absorb the urea fertilizer carried by rainwater and irrigation in agriculture. Synthesis of superabsorbent nanocomposite with free radical polymerization method used acrylic acid and acrylamide as monomer, N’N-methylene-bis-acrylamide as crosslinker, and bentonite as inorganic compound.
2. Materials and methods

2.1. Material
Rice husk used was obtained from Bogor, Indonesia. The source of rice husk was similar with the previous research [7]. Toluene-ethanol (Merck) was used to extract the cellulose from rice husk; hydrogen peroxide (Merck), and potassium hydroxide (Merck) were used as impurity removal from rice husk cellulose; acrylic acid, and acrylamide (Nippon Shokubai) were used as monomer; potassium persulphate (KPS; Merck) as initiator; \(N,N'\)-methylenebis-acrylamide (MBA, Sigma) as crosslinking agent, urea (Merck) was used as the absorbate and bentonite as inorganic compound.

2.2. Isolation of cellulose from rice husk
The isolation of rice husk cellulose was performed by the method proposed by Fan et al. [7] and Helmiyati and Kurniawan [8]. Rice husk was washed with warm water to remove impurities and water soluble substances. The rice husk was extracted with mixture of toluene: ethanol at ratio of 2:1 for 6 h, then dried at 50°C for 24 h. Hemicellulose and lignin was removed by \(\text{H}_2\text{O}_2\) 4% solution with higher concentration than previous work [9], pH of solution was set at 12 with 4% KOH. The precipitate was washed with aquadest to neutral and dried at 50°C for 24 h.

2.3. Superabsorbent synthesis
Synthesis of polymer was based on experiment performed by Spagnol et al. [10]. First, the dissolution process of rice husk cellulose was performed referred to Wu et al. [11], in which the rice husk cellulose was dissolved in 7% sodium hydroxide solution and 12% urea. The solution of cellulose was fed into a three neck flask reactor, equipped with reflux condenser and nitrogen gas. The reactor was placed in water bath at 70°C. Then, the potassium persulfate, acrylic acid, acrylamide, MBA, and bentonite were fed into the reactor. The polymerization process was conducted for 2 h at 70°C. The obtained superabsorbent was washed in distilled water, ethanol and acetone for 24 h at room temperature.

3. Results and discussion

3.1. Isolation of cellulose from rice husk
Rice husk consists of cellulose, hemicellulose, lignin, and other extractive substances [8]. After the pretreatment the obtained rendement average of cellulose can be seen in table 1. From table 1, it can be seen the obtained cellulose rendement after isolation as much as 37.85%. The rendement was smaller than the previous rendement [8], due to the \(\text{H}_2\text{O}_2\) concentration rising during the lignin removing process so that the cellulose will be whiter and bright.

3.2. Characterization of cellulose by FTIR
Figure 1 shows the FTIR spectra of rice husks, isolated cellulose, and pure cellulose. Figure 1a shows infrared absorptions for rice husk, the main absorption band shows the functional groups of rice husk at 1724 cm\(^{-1}\) (C=O stretching vibration). This is specific band for lignin [8]. The spectrum 1b does not show an absorption band at wavenumber 1724 cm\(^{-1}\). It indicates that the lignin in the isolated cellulose has been partially removed from rice husk. It can be also observed that spectrum of pure cellulose 1c is similar to the spectrum of rice husk cellulose in spectrum 1b.

| Table 1. Average rendement of cellulose isolation. |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Rice husk (g) | Dewaxing (g) | Delignification (g) | Rendement(g) | Rendement (%) |
|----------------|----------------|---------------------|---------------|---------------|
| 10.00          | 9.50           | 5.30                | 3.75          | 37.5          |
| 10.00          | 9.60           | 5.20                | 3.82          | 38.2          |
| Average        | 9.55           | 5.25                | 3.78          | 37.85         |
Figure 1. Spectra FTIR of (a) rice husk, (b), isolated cellulose and (c) pure cellulose.

Figure 2. Micrograph of (a) rice husk and (b) rice husk cellulose.

Figure 3. Diffraction patterns of pure cellulose (a) rice husk cellulose and (b) superabsorbent nanocomposite.

3.3. Characterization of cellulose by SEM

Figure 2 shows the surface morphology. In figure 2a, it can be seen that the surface morphology of rice husk surface is rough and uneven, showing that lignin and other compounds were covered the surface of cellulose. While on the isolated cellulose of rice husk in figure 2b, the fibrils of cellulose can be clearly seen. This is because after the isolation process, lignin, hemicelluloses, and other substances were removed from the isolated cellulose.
3.4. Characterization by XRD
Figure 3 shows diffraction pattern. In figure 3a, it can be seen the diffraction pattern of pure cellulose (a) and rice husk cellulose (b) have similarity with sharp peak 22.48° as intensity of crystalline and the peak at 18.25° as intensity of amorphous. The size of cellulose crystal that calculated by Scherrer’s law was 34.6 nm, which indicated nanocrystal size. Figure 3b shows that the diffraction pattern of superabsorbent indicated the amorphous structure. The amorphous structure of the superabsorbent will increase the swelling capacity, due to superabsorbent with the amorphous structure has an irregular composition, so the solution would be easy to get in and bind with the superabsorbent.

3.5. Swelling capacity
The swelling capacity of superabsorbent in urea and water are shown in figure 4. Figure 4 shows the swelling capacity of superabsorbent cellulose-poly (AA-co-AM) with bentonite and without bentonite in urea solution (a) and water (b). The swelling capacity was directly proportional towards the time, where the superabsorbent capacity will increase exponentially with time. The result of swelling capacity shows that superabsorbent of isolated cellulose with bentonite have the highest swelling capacity in urea and water. The maximum swelling capacity of isolated cellulose superabsorbent in urea and water were 611.700 g/g and 451.303 g/g, respectively.

4. Conclusions
Cellulose was successfully isolated from rice husk at 37.85% and has been characterized by FTIR, SEM, and XRD. Superabsorbent of cellulose rice husk graft poly(acrylic acid-coacrylamide)/bentonite has been synthesized successfully and characterized by XRD. The diffraction pattern of XRD indicated that cellulose was nanocrystal with the size of 34.6 nm and the diffraction pattern of superabsorbent indicated the amorphous structure. The result of swelling capacity shows that superabsorbent of isolated cellulose with bentonite have the highest swelling capacity in urea and water. The swelling capacity of superabsorbent with the highest value was the superabsorbent isolated cellulose with bentonite in urea and water with value of 611.700 g/g and 451.303 g/g, respectively.

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