Cellulose extracted from water hyacinth and the application in hydrogel

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Abstract. This paper presents the conversion of cellulose based on water hyacinth into hydrogel. The water hyacinth cellulose was prepared using acid-alkaline treatment and bleaching. The cellulose properties were optimized by varying the extraction condition such as solvent concentration and temperature. The analysis method of FTIR and XRD were used for characterizing the functional groups and crystallinity of cellulose. The effective condition of extraction were achieved at solvent concentration 17.5% w/w of NaOH, 8% v/v of H2O2 as bleaching agent and temperature of 80°C. The extracted cellulose was used to produced hydrogels using polyvinyl alcohol and glutaraldehyde as crosslinker agent. The research revealed that adding of glutaraldehyde with ratio 1:2 at 25°C give the highest water absorption capacity of 285%.

1. Introduction
Cellulose is a natural polymer that have been used in a wide range of application due to its own advantages such as readily available, non-toxic, biocompatible, hydrophilic and biodegradable[1,2]. Cellulose from natural sources have main potential application in production of biodegradable membranes, filters, adsorbent, etc. [3]. Cellulose is composed of β-1,4-glucosidic bond contains lignocellulosic fibers which are formed by lignin, hemicellulose and cellulose [4]. Cellulose biomass can be derived from wood and nonwood biomass with chemical or physical extraction process that carried out to break the complex lignocellulosic bond without destruction of the cellulose fibrils [5]. One of natural sources that contain high cellulose (10% lignin, 33% hemicellulose and 25% cellulose) is water hyacinth.

Water hyacinth (Eichhornia crassipes) is an aquatic weed species that grow rapidly and form thick layer on whole water surface [6]. Its rapid growth cause particular impacts on open water bodies such as clogging irrigation and hydropower systems, limiting livestock access to water, blocking water rivers and canals, removing native aquatic plants, changing water condition (oxygen level, pH and temperature) and reducing sunlight infiltration [7]. Water hyacinth removal by chemical, mechanical and biological method requires a huge amount of money and provide detrimental effect on the water environment like destruction of other useful plants and environmental pollution. However, water hyacinth is rich in cellulose content and easily converted chemically into useful derivative product and make this species an excellent candidate for cellulose base natural polymers. In this project cellulose fiber from water hyacinth was extracted according to method of Hu [12] with some modification including hydrolysis, delignification, pulping and bleaching.
Hydrogel is defined as polymeric material with three-dimensional structure capable of absorbing and releasing large amount of water. Nowadays, the application of hydrogels has been widely used in various industries such as cosmetics, food industry and drug delivery system. Compared to hydrogels made from synthetic polymers, hydrogels from natural materials such as starch, chitosan and cellulose have more superiority properties such as good biocompatibility, biodegradable, good permeability, low friction and toxicity factor [8]. Due to these superiority, the development of hydrogel from cellulose is promising for application to the pharmaceutical and biomaterial field. Superabsorbent hydrogel obtained by chemical or physical crosslinking between polymer and crosslinker agent [9]. Recently, other natural source of cellulose have been studied in the hydrogels production such as rice husk [9]; oat husk [4]; bamboo shoot [2]; pineapple peel [1]; tea residue [11]. However, the application of cellulose from water hyacinth as hydrogel feed stock has not been reported. In this study, cellulose fibers from water hyacinth was isolated and characterized and used to produce hydrogels.

2. Methodology

2.1. Material
Water hyacinth was collected from Kulon Progo coast in Yogyakarta and dried under the sunlight for 3 days. 99.8% ethanol, 99.9% toluene, acetic acid, nitric acid, sodium hydroxide, sodium sulphite, hydrogen peroxide, sodium hypochlorite, hydrochloric acid and glutaraldehyde as crosslinker agent were purchased from Merck and Sigma-Aldrich.

2.2. Cellulose fiber isolation
Firstly, the stem of water hyacinth were washed, dried under the sunlight for 3 days, grinded and sieved through a 40 mesh sieve. The dried stem was then mixed with ethanol and toluene for dewaxing process at 75°C for 6 h. After dewaxing, the sample hydrolyzed with HNO3 solution 3.5% (v/v) at 90 °C for 2 h. For removal of the lignin, an alkaline treatment with Na2SO3 solution (2% w/v) and NaOH solution (2% w/v) was carried out using magnetic stirrer at 50°C for 1 h. Furthermore, bleaching process using various type of solvent (H2O2 10%, NaOCl 8% and HCI 3% v/v) was performed for remaining lignin and hemicellulose removal and stirred at 60°C for 15 minutes.

2.3. Preparation of hydrogel
Hydrogel was prepared from water hyacinth cellulose referring the method of Oliveira [4]. The cellulose was dissolved into NaOH solution (8.5% w/v) until the uniform viscous mixture was obtained and frozen for 24 hours. Furthermore, the mixture was melted and mixed with (2%, 4% and 6%) wt crosslinker agent (glutaraldehyde or poly vinyl alcohol) and stirred for 4 h to avert bubble formation. A sample of the gel was then casted onto a acrylic plate and placed in oven at 50°C for 6 h.

2.4. Cellulose fiber and hydrogel characterizations
Functional groups of cellulose fiber and hydrogel were investigated by Fourier Transform Infrared Spectrometer (FT-R). X-ray diffraction (XRD) were performed to analyzed relative crystallinity of the cellulose and hydrogel. The swelling capacity of the hydrogels was evaluated in distilled water by measuring the weight of samples before and after soaked in water at 4°C, 25°C and 50°C for 24 h. The swelling ratio of the hydrogel was performed according to the equation:

\[ SR = \frac{W_s - W_d}{W_d} \times 100 \]  

Where \( W_d \) is the weight of initial dried sample and \( W_s \) is the weight of the swollen hydrogel.

3. Result and discussion

3.1. Characterization and extraction yield of cellulose
3.1.1. FTIR and XRD analysis on extracted cellulose fibre. The comparison of functional groups of cellulose extracted from water hyacinth with different solvent were presented in Figure 1. From figure
1, it was observed that the samples with H$_2$O$_2$ solvent exhibited the absorption peak around 3447.65 cm$^{-1}$ and 2901.37 cm$^{-1}$ were related to the $\text{–OH}$ and $\text{C-H}$ stretching vibration. The spectra of extracted cellulose also showed a band at 1161.5 cm$^{-1}$ and 1112.88 cm$^{-1}$ which more intense than the band exhibited by raw water hyacinth. The same phenomenon was reported in isolation of cellulose from oat and rice husk carried out by Oliveira [4]. According to Halal [13], the band at 1161.5 cm$^{-1}$ indicate of C3 carbon vibrations and the band at 1319.44 cm$^{-1}$ indicate the vibration of the glycosidic C-O-C bond on cellulose fibers. The presence of functional groups of cellulose constituent components was also seen with the appearance of bands at 1060.7 and 893.79 cm$^{-1}$ which related to C-O and C-H stretching vibration, in which spectra of cellulose fibres exhibited greater absorption peak resolution compared to peak from raw material [14].

Based on the FTIR analysis, the final result of extraction with H$_2$O$_2$ solvent still represent character of cellulose by presence of O-H, C-H, C-O and C-H stretching vibration. However, the band at 893.79 cm$^{-1}$ shows that the cellulose contained $\beta$-cellulose which insoluble at NaOH concentration below 17.5\% wt. The absorption peak at 1637.96 cm$^{-1}$ was related to the C=O stretching vibration of carboxylate ions. According to Zhang [15], a number of carboxylic groups were produced due to the presence of oxidizing agents (HNO$_3$) during extraction process of cellulose. According to Hassan [16] the bands at 1500-1600 cm$^{-1}$ are associated to the presence of aromatic ring and carbonyl groups which indicate the lignin constituent structure. While the absorption peak around 1700 cm$^{-1}$ can be assigned to the acetyl and ester functional groups as part of the lignin compound. From figure 1, it is confirmed that lignin and hemicellulose constituent were completely removed during delignification and pulping process.

![Figure 1. FTIR spectra of the cellulose of water hyacinth.](image)

The X-ray diffraction which present relative crystallinity of the raw water hyacinth and cellulose fibers are presented in Figure 2 and Figure 3, respectively. The XRD pattern of raw material was found exhibiting the peaks around 15.3°, 21.2°, 33.4° which indicate the characteristics of lignocellulosic materials. The extracted cellulose showed the peaks around 17.8°, 21.2°, 34° due to its crystal structure. The relative crystallinity of raw material was found lower compared to the cellulose which evidenced that the removal of lignin and hemicellulose promote an increasing crystallinity ratio. According to Abraham [17], the presence of cellulose caused crystallinity of lignocellulose, which has a crystal structure. In the other hand, another component including lignin and hemicellulose are amorphous. In
addition, the crystallinity affects the swelling ratio of hydrogels, because the higher crystallinity the higher water absorption capacity of hydrogels.

3.1.2. Extraction yield of extracted cellulose fibers. The yield of the cellulose from water hyacinth with different solvent are shown in Table 1. In this work, the highest percentage of mass reduction was found in hydrolysis step compared to another steps in cellulose extraction process. This is because hemicellulose has short chain and can be hydrolysed easily using nitric acid (HNO₃) compared to cellulose and lignin, therefore the acids can break the hemicellulose polymers into simple monomers. It was also observed that difference result obtained between NaOCl and H₂O₂ as solvents in bleaching process, where the highest percentages of mass reduction obtained with the variation of NaOCl. NaOCl has strong chemical content that can degrade cellulose in high amount. On the other hand, the lowest percentages of mass reduction was found in bleaching process with H₂O₂ as solvent, it can be caused by the H₂O₂ characteristic that tends not to damage cellulose and more environmentally friendly. The cellulose yield of the water hyacinth was 12.45 g cellulose/100 g of water hyacinth.

| Steps of cellulose extraction process | Percentage of mass reduction (%) |
|--------------------------------------|----------------------------------|
| H₂O₂                                 | NaOCl                            | HCl     |
| Dewaxing                             | 32.13                            | 31.07   | 32.27   |
| Hydrolysis                           | 60.03                            | 62.60   | 67.83   |
| Delignification                      | 15.75                            | 23.40   | 15.47   |
| Pulping                              | 10.35                            | 12.86   | 6.74    |
| Bleaching                            | 5.90                             | 18.90   | 10.34   |
| **Yield** (g cellulose/100 g water hyacinth) | 12.45                            | 8.95    | 10.76   |

3.2. Characterization of hydrogel

3.2.1. FTIR analysis on hydrogel. Figure 4 shows the FTIR characteristic of hydrogel prepared using glutaraldehyde and poly vinyl alcohol as crosslinker agent. The spectra of hydrogels with glutaraldehyde showed band at 3302 cm⁻¹ can be assigned to the stretching of –OH, while the absorption band at 2935 cm⁻¹ is associated to the stretching of the aldehyde groups. The absorption band at 1705 cm⁻¹, which is related to the C=O and C-O stretching of carboxylate groups.

The spectra of hydrogels with poly vinyl alcohol shows the absorption peak at 2915 cm⁻¹ and 3318 cm⁻¹ are respectively related to the C-H stretching of methyl in cellulose and O-H stretching in the cellulose molecule chain, while the peak at 2916 cm⁻¹ is related to the PVA alkyl groups stretching. The band at 1724 cm⁻¹ was due to the contribution of the C=O and C-O stretching vibration in carboxyl groups. According to Oliveira, the interaction between cellulose and poly vinyl alcohol was affirmed by the band around 1076 cm⁻¹ associated with C=O, where in the PVA spectrum was more intense.
Figure 4. FTIR spectra of the hydrogel using glutaraldehyde and polyvinyl alcohol.

3.2.2. Swelling Capacity. The swelling capacity of hydrogels observed at various additive concentration and temperature. Table 2 shows analyzed swelling ratio result of the hydrogel which soaked in distilled water at temperature 25°C. These result indicate that the higher glutaraldehyde concentration exhibited significant lower equilibrium swelling ratio (ESR). This might occur due to the uniform and compact structure do not form during hydrogel formation and the hydrogels have bigger micrometer pores. Water is absorbed and restricted in the structure of hydrogel through smaller micrometre pores and swelling ratio depends on the size of pores. This phenomenon is similar to the polyvinyl alcohol addition as additive, however, compared with PVA, addition of glutaraldehyde showed that hydrogel preserved more water in their three-dimensional structure.

Table 2. Swelling capacity of hydrogel at different additive concentration.

| Additive        | Ratio | ESR % |
|-----------------|-------|-------|
| Glutaraldehyde  | 1:2   | 285   |
|                 | 1:4   | 234   |
|                 | 1:6   | 202   |
| Poly vinyl alcohol | 1:2  | 186   |
|                 | 1:4   | 110   |
|                 | 1:6   | 128   |

From table 3, it was found that swelling capacity increase with increasing temperature up to 30°C, and significantly decrease at temperature 45°C for both additive addition. At temperature, the chain movement on the hydrogel matrix was occurred due to formation of hydrogen bond from water molecules which has polar functional group. However, at high temperature these structure decrease due to the breakage of hydrogen bonds between chains on the matrix and water molecules.
Table 3. Swelling capacity of hydrogel at temperature.

| Additive              | Temperature, °C | ESR % |
|-----------------------|-----------------|-------|
| Glutaraldehyde        | 15              | 256   |
|                       | 25              | 285   |
|                       | 35              | 298   |
|                       | 45              | 195   |
|                       | 50              | 212   |
| Poly vinyl alcohol    | 15              | 115   |
|                       | 25              | 186   |
|                       | 35              | 173   |
|                       | 45              | 124   |
|                       | 50              | 122   |

3.2.3 Maximum stress compression. The mechanical properties of hydrogel was investigated by measuring the allowable maximum stress during compression. The hydrogel prepared from cellulose with glutaraldehyde as crosslinker agent had lower maximum stress compression compared to hydrogel with poly vinyl alcohol. This result obtained due to the poly vinyl alcohol can lead an increasing of crystalline structure within hydrogel network which effected in strength of hydrogel. Some papers which studied the mechanical behaviour of hydrogel reported that the hydrogen bond between functional groups of polymer chain in hydrogel network are broken during the first compression reducing hydrogel stiffness [18]. These result revealed that hydrogel based on poly vinyl alcohol and cellulose was more impervious to force applied during compression. Therefore it is suggested that a stable network was formed [19].

Table 4. Maximum stress compression of hydrogel.

| Additive              | Ratio | Maximum stress compression |
|-----------------------|-------|----------------------------|
| Glutaraldehyde        | 1:2   | 1.8 kPa                    |
|                       | 1:4   | 1.56 kPa                   |
|                       | 1:6   | 1.88 kPa                   |
| Poly vinyl alcohol    | 1:2   | 2.67 kPa                   |
|                       | 1:4   | 3.15 kPa                   |
|                       | 1:6   | 2.89 kPa                   |

4. Conclusion
Hydrogel prepared from water hyacinth cellulose exhibite different structural, crystallinity, absorption capacity and maximum stress compression depend on the type of additive. The application of glutaraldehide (1:2) produce hydrogel with high swelling capacity (285%) at 25°C, while the highest maximum stress compression (3.15 kPa) was presented by hydrogel prepared with poly vinyl alcohol (1:4) as additive.

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