Characterization and properties of sodium alginate from brown algae used as an ecofriendly superabsorbent

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Abstract. Sodium alginate obtained from the extraction of brown algae is used as the backbone for the synthesis of superabsorbent nanocomposite copolymerization. The first stage of extraction is the demineralization process using 0.1 M HCl solution and then 2% Na2CO3 solution for 2 hours at 60°C. The rendement of sodium alginate obtained was 44.32% with molecular weight of 40680 g/mol with measurement of the intrinsic viscosity. FTIR spectra of sodium alginate showed mannuronic acid functional group at wavenumber 884 cm⁻¹ and the uronic acid at wavenumber 939 cm⁻¹, OH functional group at wavenumber 3200-3400 cm⁻¹, and CH₂ stretching at wavenumber 2928 cm⁻¹. The diffraction pattern of isolated sodium alginate has specific 2θ at 13.068 and 21.096, amorphous intensity found specific 2θ at 18.058, and the obtained crystallinity degree of the sodium alginate is equal to 29.292% from the XRD analysis. The morphological analysis by SEM shows fibrils of isolated sodium alginate. The success isolation of sodium alginate from brown algae is supported by DSC which shows the decomposition temperature of pure sodium alginate and isolated alginate have close values, namely 251.12°C for pure sodium alginate and 229.90°C for isolated sodium alginate.

Keywords: sodium alginate, nanocomposite, brown algae, copolymerization

1. Introduction
Alginates naturally present in brown algae cell walls [1, 2]. Alginates are polysaccharides found in brown algae, composed mainly by linear polymers of β-(1-4)-D-mannuronic (M), and α-L-gluronic (G) acids, which are different in terms of their proportions and linear arrangements [3, 4]. The sequence of monomers (M, G) changes greatly depending on the source [5]. In brown algae, alginates are the most abundant polysaccharides reaching up to 40% of the dry weight [6]. Amongst the recent applications of alginates, we can highlight their use as a matrix to encapsulate and release fertilizer and also for the synthesis of superabsorbent [7-9]. Alginates are typically described by their M/G ratio and average molecular weight, since these parameters are closely related to the functionality of the alginates as the encapsulation material [10]. Generally, the extraction and purification processes of alginates are based on the conversion from the insoluble form in the algae cell walls to the soluble one, normally by the sodium salt, followed by successive dissolutions and precipitations to eliminate impurities [11].

In this research, sodium alginate has been isolated from brown algae with acetone-methanol and chloroform, and can be separated from pigments, fat and other extractive substances. Then, the success isolation of the sodium alginate was observed by the molecular weight, and characterization by SEM, FTIR, XRD and DSC.
2. Materials and methods

2.1. Materials
Brown algae that used in this work, was obtained from Banten, Indonesia. Methanol (Merck), Acetone (Merck), and Chloroform (Merck) were used to remove pigment and fat from brown algae. Chloride Acid (Merck) was used to demineralize brown algae, Sodium Carbonate (Merck) to dissolve the alginate in the form of sodium salt, potassium hydroxide (Merck) as bleaching and impurity removal from brown algae. Ethanol (Merck) was used to precipitate the sodium alginate.

2.2. Sodium Alginate Isolation from Brown Algae
Isolation of the sodium alginate from brown algae referred to Sellimi et al. [12] with slight modifications. Brown Algae (50 g) was depigmented and defatted sequentially with acetone-methanol (7 : 3) and chloroform for 24 h at 30°C under constant stirring. The rendement was treated at pH around 2.0 with HCl solution for 2 h at 60°C under constant stirring for demineralization process. The supernatant was eliminated by centrifugation then the residue was washed with distilled water and treated with 2% Na2CO3 at 60°C for 2 h under constant stirring to form sodium alginate, followed by the solution bleaching with H2O2. The rendement was purified with methanol and acetone and then dried at room temperature. Sodium Alginate was analyzed by FTIR, XRD, SEM, and DSC and compared with the standard sodium alginate.

3. Results and discussion

3.1. Rendement of sodium alginate from brown algae
After the pretreatment process, the obtained average yield of sodium alginate can be seen in table 1. It can be seen the rendement of sodium alginate obtained after isolation is 44.32%.

| Mass of Brown Algae (g) | Mass of Sodium Alginate (g) | Yield (%) |
|------------------------|-----------------------------|-----------|
| 25.00                  | 11.13                       | 44.52     |
| 25.00                  | 11.03                       | 44.12     |
| Average                |                             | 44.32     |

3.2. Molecular weight determination
The average molecular weight (M) was calculated from the Mark-Houwink equation:

\[ [\eta] = k M^a \]  \hspace{1cm} (1)

where \([\eta]\) is the intrinsic viscosity, and the constants \(a\) and \(k\) are empirical parameters which are depended on the system (polymer, solvent, and temperature). The obtained intrinsic viscosity in 0.1 M NaCl at 25°C for the isolated sodium alginate was 81.932 cm³/g, so the molecular weight of sodium alginate was 40680 g/mol.

3.3. Analysis of functional groups of sodium alginate by FTIR
The FTIR spectra of the isolated sodium alginate showed in curve a and pure sodium alginate in curve b (figure 1). Both spectra have the similarities in which FTIR spectra of isolated sodium alginate and standard showed mannuronic acid functional group at wavenumber 884 cm⁻¹ and the umeric acid at wavenumber 939 cm⁻¹, OH functional group at wavenumber 3200-3400 cm⁻¹, and CH₂ stretching at wavenumber 2928 cm⁻¹.
3.4. Analysis of crystallinity index of sodium alginate by XRD
The XRD patterns of brown algae, isolated sodium alginate and pure sodium alginate are shown in figure 2. Figure 2a shows the diffraction pattern of brown algae. It can be seen that brown algae has an amorphous structure with a peak $2\theta = 22.89^\circ$. Figure 2b is diffraction pattern of pure sodium alginate and Figure 2c is the diffraction pattern of the isolated sodium alginate. It can be seen that both the diffraction patterns have similarities with the crystallinity index 35.62% and 29.292%, respectively. Crystallinity index of pure alginate is higher than the isolated alginate, because the purity of the isolated alginate is less than pure alginate. This shows that the pure sodium alginate and isolated alginate have semi-crystalline structure.

3.5. Analysis of surface morphology of sodium alginate by SEM
The surface morphology of brown algae and sodium alginate can be seen in figure 3. Figure 3a shows that the surface morphology of brown algae is not clearly indicating the fibrils sodium alginate and figure 3b shows the surface morphology of isolated sodium alginate indicating that the fibrils of sodium alginate fibers can be clearly observed because the impurities have been removed in the isolation process.

3.6. DSC analysis of sodium alginate
The success isolation of sodium alginate was supported by DSC and can be seen in figure 4. Figure 4a is thermogram from pure sodium alginate and figure 4b is thermogram from isolated sodium alginate. It can be seen that the decomposition temperature of pure sodium alginate and isolated alginate have value of 251.12°C for pure sodium alginate and 229.90°C for the isolated sodium alginate. The decomposition temperature value of pure sodium alginate is higher than isolated sodium alginate because the crystallinity index of pure alginate is higher than the isolated alginate, as obtained from the XRD diffraction patterns that have been discussed.
Figure 3. Micrograph of (a) brown algae and (b) sodium alginate isolation

Figure 4. DSC thermogram of (a) pure sodium alginate and (b) isolated sodium alginate

4. Conclusions
Isolation of sodium alginate from brown algae has been successfully performed. The obtained rendement of sodium alginate was 44.32% with molecular weight of 40680 g/mol. This successful process was supported by FTIR spectra which showed mannuronic acid functional group at wavenumber 884 cm\(^{-1}\) and uronic acid at wavenumber 939 cm\(^{-1}\). The diffraction patterns of the isolated and pure sodium alginate have similarities with the crystallinity index of 35.62% and 29.292%, respectively. It showed that the pure and isolated sodium alginate have semi-crystalline structure. The surface morphology of the isolated sodium alginate analyzed by SEM showed that the fibrils of sodium alginate fibers can be clearly seen because the impurities have been removed in the isolation process. By the support of DSC the decomposition temperature of pure sodium alginate and isolated alginate showed close values, namely 251.12°C for pure sodium alginate, and 229.90°C for isolated sodium alginate.

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References
[1] Fertah M, Belfkira A, Dahmane E M, Taourirte M and Brouillette F 2014 Extraction and characterization of sodium alginate from Moroccan *Laminaria digitata* brown seaweed *Arabian Journal of Chemistry* http://dx.doi.org/10.1016/j.arabjc.2014.05.003
[2] Larsen B, Salem D M, Sallam M A, Mishrikey M M and Beltagy A 2003 *Carbohydr. Res.* 338 2325-36
[3] Torres M R, Sousa A P A, Filho E A T S, Melo D F, Feitosa J P A, de Paula R C M and Lima M G S 2007 *Carbohydr. Res.* 342 2067-74
[4] Sharma A and Gupta M N 2002 *Carbohydr. Polym.* 48 391-5
[5] Donati I, Vetere A, Gamini A, Skajak-Braek G, Coslovi A, Campa C and Paoletti S 2003 *Biomacromolecules* 4 624-31
[6] Moe S T, Draget K I, Skajak-Braek G and Smidsrod O 1995 *Food Polysaccharides and Their Applications* ed A M Stephen (New York: Marcel Dekker) pp 245-86

[7] Zhang Y, Liang X, Yang X, Liu H and Yao J 2014 *ACS Sustainable Chem. Eng.* 2 1871-8

[8] Rashidzadeh A and Olad A 2014 *Carbohydr. Polym.* **114** 269-78

[9] Rashidzadeh A, Olad A and Reyhanitabar A 2015 Hydrogel/clinoptilolite nanocomposite-coated fertilizer: swelling, water-retention and slow-release fertilizer properties *Polym. Bull.* **72** DOI 10.1007/s00289-015-1428-y

[10] Finotelli P V, Da Silva D, Sola-Penna M, Rossi A M, Farina M, Andrade L R, Takeuchi A Y and Rocha-Leao M H 2010 *Colloids Surf.* B **81** 206-11

[11] Rinaudo M 2008 *Polym. Int.* **57** 397-430

[12] Sellimi S, Kadri N, Barragan-Montero V, Laouer H, Hajji M and Nasri M 2014 *Int. J. Biol. Macromol.* **66** 281-8