

Utilization of Shrimp Skin Waste (Sea Lobster) As Raw Material for the Membrane Filtration

Ni Nyoman Rupiasih^{1,*}, Made Sumadiyasa², Hery Suyanto², Putri Windari¹

¹Biophysics Laboratory, ²Applied Physics Laboratory, Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Denpasar, 80361, Indonesia

* E-mail: rupiasih@gmail.com

Abstract. In view of the increasing littering of the sea banks by shells of crustaceans, a study was carried out to investigate the extraction and characterization of chitosan from skin waste of sea lobster i.e. 'Bamboo Lobster' (*Panulirus versicolor*). Chitosan was extracted using conventional methods such as pretreatment, demineralization, deproteinization, and deacetylation. The result showed that the degree of deacetylation of chitosan obtained is 70.02%. The FTIR spectra of the chitosan gave a characteristic of $-NH_2$ band at 3447 cm^{-1} and carbonyl group band at 1655 cm^{-1} . This chitosan has been used to prepare membrane. The chitosan membrane 2% has been prepared using phase inversion method with precipitation by solvent evaporation. The membranes were characterized by FTIR spectrophotometer, *Nova 1200e* using BJH method, and filtration method. The results show that thickness of the membrane is about $134\text{ }\mu\text{m}$. The FTIR spectra show that functional groups present in the membrane are $-NH$, $-CH$, $C=O$, and $-OH$. Using BJH method obtained that the pore diameter is 3.382 nm with pore density is $8.95 \times 10^5\text{ pores/m}^3$. By filtration method obtained that pure water flux (PWF) of the membrane are 386.662 and $489.627\text{ l/m}^2\cdot\text{h}$ at pressure $80\text{-}85\text{ kPa}$ and $90\text{-}100\text{ kPa}$, respectively. These results show that skin waste of sea lobster was discovered as a raw material to prepare chitosan membrane. The membrane obtained is belonged to mesoporous group which may use in microfiltration process.

1. Introduction

The processing of frozen lobster will produce solid waste, namely skin and head. During the time, solid waste is not fully utilized, which are usually thrown into the sea or just left on the edge of the beach. This create problem that must be faced by the community, especially coastal communities. In terms of the usefulness of such waste the parts that can be further harnessed into useful products, such as chitin and chitosan.

Chitin is the second most abundant polysaccharide (next to cellulose) synthesized by a large number of living organisms [1]. In nature, chitin is found as structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast. It is also produced by a number of other living organisms in the lower plant and animal kingdoms. Meanwhile, chitosan is produced only by some fungi from the family *Mucoraceae* [2].

Chitin is a high molecular weight linear homopolymer of β -(1,4) linked N-acetylglucosamine (Nacetyl-2-amino-2-deoxy-D-glucopyranose) units. Chitin samples contain a high content of N-acetylglucosamine units; hence, they are insoluble in water and common organic solvents. On the other hand, they dissolve only in solvents such as *N,N*dimethylacetamide, hexafluoroacetone or hexafluoro-2-



propanol. Chitosan, a copolymer of glucosamine and N-acetyl glucosamine units linked by 1-4 glucosidic bonds, is a cationic polysaccharide [3,4].

Industrially, chitosan is usually produced by de-N-acetylation of chitin. When the degree of N-acetylation is less than 50%, chitin becomes soluble in aqueous acidic solutions (pH < 6.0) and is called chitosan [3,4,5]. This means that chitosan represents a group of fully and partially deacetylated chitins, but a rigid nomenclature with respect to the degree of N-deacetylation between chitin and chitosan has not been established [6].

Chitin and chitosan have great economic value because of their versatile biological activities such as biocompatibility, biodegradability, non-toxicity and adsorptive abilities, as well as chemical applications, mainly in the medical and pharmaceutical fields [7,8,9]. The biological properties of these compounds depend closely on their physicochemical parameters, especially their solubility in water and other commonly used solvents.

The purpose of this study was to isolate chitosan from skin waste of sea lobster that is 'Bamboo Lobster' (*Panulirus versicolor*). The product was used as a matrix material to synthesize filtration membrane.

2. Basic Theory

2.1. Extraction and Characterization of Chitosan

The Bamboo Lobster (*Panulirus versicolor*) skin waste was obtained from Serangan, Bali. The chitosan extraction was done in four steps such as pretreatment, demineralization, deproteinization and the deacetylation. The skin waste was washed thoroughly with demineralized water (aqua-dm) and dried in an oven at 35°C, then ground and sieved. One hundred gram of the sample was taken for the extraction process. The demineralization step is the sample were soaked in 1M HCl (1:15 w/v) at 70-80°C for 4 h and stirred it at ± 50 rpm. After which it was washed in acid until no bubbles were seen and no colour changing was observed. The sample washed with aqua-dm until a relatively neutral pH obtained and dried in the oven at 70°C for 24 h. The deproteinization step is the demineralized dried sample were weighed and soaked in NaOH 3.5% solution (1:10 w/v) at 65-70°C for 4 h, stirred it at ± 50 rpm. Then the samples washed thoroughly with water followed by aqua-dm until a neutral pH obtained. The chitin was then dried and weighed. The deacetylation step is the chitin was deacetylated with NaOH 60% (1:20 w/v) for 4 h at 120°C to get chitosan. The chitosan obtained washed thoroughly with water followed by aqua-dm then dried at 70°C for 24 h. The dried chitosan is ready to characterize or use. The characterization was done by Fourier transformed infrared (FTIR) spectrophotometer (IR Prestige 21) in the range of 400 to 4000 cm^{-1} . The spectra of chitin and chitosan are shown in Figures 1.

2.2. Preparation of Chitosan Membrane

The chitosan solution of 2% (w/v) was prepared by dissolving 5 g of the chitosan powder that obtained in 250 ml of 1% acetic acid solution. The mixture was stirred for ± 4 h at room temperature to obtain dope solution. The dope solution was casted in a glass plate and dried at room temperature for 6 days. The chitosan membrane 2% obtained was dipped in NaOH 1% solution, washed with aqua-dm 3 times to eliminate the excess of NaOH, and then dried. The thickness of the membrane obtained was around 134 μm .

2.3. Characterization of Chitosan Membrane

In this study, the chitosan membrane has been characterized by FTIR spectrophotometer (IR Prestige 21), *Quantachrome instruments Nova 1200e (gas sorption analyzer versions 10.05)* by BJH method and filtration method.

Filtration Studies of Chitosan Membrane

The measurement of pure water flux (*PWF*) was performed using *dead-end* filtration method with variation in pressure 90-100 kPa and 80-85 kPa. Membranes in the form of circles, each of diameters approximately 4 cm, were cut from the dried membranes. The effective surface area of the membrane is around $1.023 \times 10^{-3} \text{ m}^2$. They were kept in distilled water (DW) for around 5 minutes before being used as a filter. The *PWF* was calculated using formula 1 [10].

$$\text{Flux}(J) = \frac{V}{At} \quad (1)$$

Where *V* is volume of permeate, in *l*; *A* is area of the membrane in m^2 ; and *t* is time in h.

3. Results and Discussion

3.1. Characteristics of Chitin and Chitosan

Figure 1 shows FTIR spectra of the chitin and chitosan. The FTIR spectra gave characteristic bands of -NH_2 at around 3447 cm^{-1} and carbonyl group at around 1655 cm^{-1} . The degree of deacetylation (DD) was calculated using equation (2) by Domszy dan Robers (2008) [11]. The wavenumber used are 1655 and 3450 cm^{-1} .

$$DD = \left[1 - \left[\frac{A_{1655}}{A_{3450}} \times \frac{1}{1,33} \right] \right] \times 100\% \quad (2)$$

Where A_{1655} and A_{3450} are the absorbance at wavenumber of 1655 cm^{-1} and 3450 cm^{-1} , respectively. The degree of deacetylation (DD) of chitosan obtained is 70.02% .

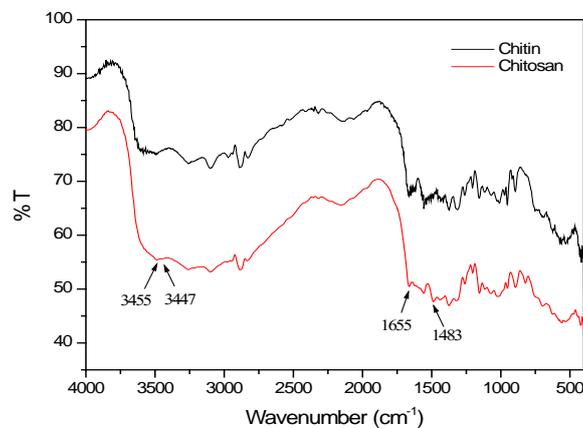


FIGURE 1. FTIR spectra of Chitin and Chitosan.

3.2. Characteristics of Chitosan Membrane

3.2.1 FTIR Characteristics of Chitosan Membrane

The FTIR spectrum of chitosan membrane is presented in Fig. 2. The characteristic absorption of the chitosan is a band at around 3310 cm^{-1} which is assigned to the NH bending and OH stretching vibration of amino group. A band at around 2884 cm^{-1} is assigned to vibration of C-H stretching. A band at around 1666 cm^{-1} and 1564 cm^{-1} are due to C=O amida and N-H, respectively [3,12,13].

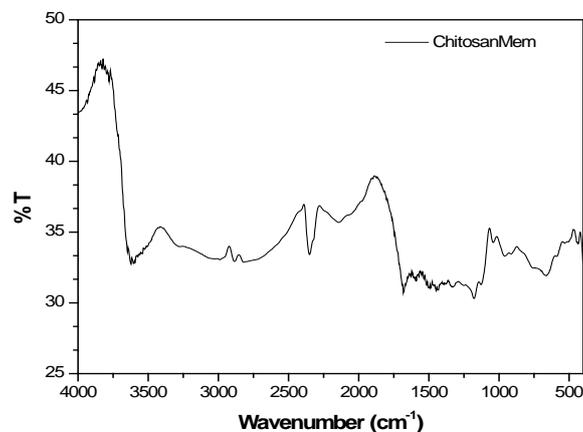


FIGURE 2. The FTIR spectrum of Chitosan biomembrane.

3.2.2 Pore Structure of Chitosan Membrane by BJH Method Using Nova 1200e

The physical characteristics of pore structure of the membrane obtained using *Quantachrome instruments Nova 1200e* (any gas sorption analyzer versions 10.05) by BJH method. The results obtained

are the surface area, pore volume, pore diameter, pore number, and pore density of chitosan membrane 2% which is presented in Table 1.

TABLE 1. The surface area, pore volume, pore radius, pore number, and pore density of chitosan membrane 2% obtained by *Nova 1200e* using BJH method.

| Membrane | Surface Area (m ² /g) | Pore Volume (cc/g) | Pore Diameter (nm) | Pore Number (pores/g) | Pore Density (pores/m ³) |
|----------|-------------------------------------|-----------------------|-----------------------|--------------------------|---|
| 2% | 1.816 | 0.003 | 3.382 | 1.79 x 10 ⁹ | 8.95 x 10 ⁵ |

Based on IUPAC (*convention for nomenclature of porosity*, 1972), the membrane obtained is belonged to mesoporous group which may use as filtration membrane such as microfiltration [10,14].

3.2.3 Filtration Studies of Chitosan Membrane

The average value of pure water flux (*PWF*) obtained is calculated using equation (1) and the results are presented in Table 2. The result shows that *PWF* increased as increasing the pressure.

TABLE 2. The average value of pure water flux (*PWF*) for each operational pressure: 90-100 kPa and 80-85 kPa.

| Membran e | Pure Water Flux (l/m ² .h) | |
|--------------|---------------------------------------|------------------|
| | 90-100 kPa | 80-85 kPa |
| 2% | 489.627 ± 33.389 | 386.662 ± 14.779 |

4. Conclusion

From the experimental data, the study has demonstrated that skin waste of sea lobster i.e. Bamboo Lobster (*Panulirus versicolor*) was discovered as a raw material to prepare chitosan membrane. The membrane obtained is belonged to mesoporous group which may use in microfiltration process.

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