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The Extraction of Chitin from Indonesian Shells and its Potential as Zinc Ion Batteries Supporting Material

Abdillah Syah Putra[1], Irma Sulistina[1], Mutiara Febrianti[1], Nuril. M. Apdhila[1], Cornelius S. Yudha[1,2,*]

1. Chemical Engineering Department, Vocational School, Universitas Sebelas Maret, Jl. Kol. Sutarto 150K Jebres, Surakarta 57126, Indonesia
2. Centre of Excellence for Electrical Energy Storage Technology, Universitas Sebelas Maret, Jl. Slamet Riyadi 435, Surakarta 57146, Indonesia

* Corresponding author: corneliussyudha@staff.uns.ac.id
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ABSTRACT: Indonesia is an archipelagic country with a vast water area. One of the results of aquaculture in Indonesia is shrimp. Based on data from the Ministry of Maritime Affairs and Fisheries in 2022, shrimp production results amounted to 8,3 tons. This makes Indonesia one of the largest shrimp-exporting countries in Southeast Asia. The part of the shrimp often consumed by the public is the meat. So that the heads, tails, and shells that have been peeled are usually discarded. Shrimp waste, besides polluting the environment, can also disturb the comfort of local residents, so efforts are needed to overcome it. Shrimp shell contains 27.6% minerals, 34.9% protein, and 18.1% chitin. The chitin content in shrimp shells can be processed into materials for zinc-ion batteries, namely chitosan, which has non-toxic properties and can be used as polymer electrolytes with good conductivity values through the deacetylation process. The main ingredient is shrimp shell powder from cleaned and dried shrimp waste. In this study, there are three steps of procedures: the deproteination method using NaOH base solution, demineralization using HCl acid solution, and testing for chitin with the Van Wesslink color reaction. In this experiment, the yields obtained were 0.38, 0.1, 0.12, and 0.47-gram chitin/gram shrimp shell. The big difference in the yield produced is due to the different types of shrimp waste used.

Keywords: deacetylated, Indonesian, waste, chitin, shrimp

1. Introduction

Indonesia is an archipelagic country with a vast water area. One of the results of aquaculture in Indonesia is shrimp. Shrimps (Caridae) are fresh, brackish, saltwater animals. There are also various types of shrimp, such as name shrimp, Werbung shrimp, peci shrimp, giant prawns, and others. Based on data from the Ministry of Maritime Affairs and Fisheries in 2022, shrimp production results amounted to 8.3 tons [1]. This makes Indonesia one of the largest shrimp-exporting countries in Southeast Asia.

The part of the shrimp often consumed by the public is the meat. So that the heads, tails, and shells that have been peeled are usually discarded. Shrimp waste that needs to be treated properly will cause problems for the surrounding environment. Waste that is disposed of carelessly can pollute the environment, causing disease. Not only that, the smell of shrimp waste can also disturb residents' comfort. Therefore, efforts are needed to overcome the shrimp waste.

Shrimp waste is usually used as a mixture in making shrimp paste. In addition, shrimp shell contains 27.6% minerals, 34.9% protein, 18.1% chitin, and other components such as dissolved substances, fat and digestible protein of 19.4%. However, the amount of this content depends on the type of shrimp [2]. The chitin content in shrimp shells can also be processed into chitosan, which can be applied in various fields, one of which is as a material for zinc-ion batteries. Chitin can be processed into chitosan, which has non-toxic properties, can bind ions, quickly decomposes (biodegradable), and has groups of lone electron pairs that can be used as polymer electrolytes with good conductivity through deacetylation processes. The deacetylation process removes acetyl groups (-COCH3) from chitin using an alkaline solution to turn into an amine group (-NH2). Chitin has a long crystalline structure with strong hydrogen bonds between nitrogen atoms and carboxylic groups on adjacent chains [3]. Amino groups and carboxylic groups can be modified to make polymer electrolyte membranes. Electrolytic polymer membranes in batteries are helpful as a medium for ion transport (a substitute for electrolyte solution) and a separator between the cathode and anode [4].

Since chitosan has high economic value, it is essential to research how to process shrimp shells into chitin. This study used the method of deproteination, demineralization, and qualitative testing for the presence of chitin using a Van Weslink color reaction. With the conversion of shrimp shells into chitin, it is expected to have economic value and reduce environmental pollution.

2. Experimental Method

2.1 Material

The tool used is a glass beaker, stirrer bar, flask, watch glass, glass funnel, hot plate magnetic stirrer, clamps, stands, scales/balance, filters, thermometers, spoons, volumetric flasks, pipette pumps, measuring pipettes, dropping pipettes, porcelain cups, pH paper, filter paper, and measuring cups. The main ingredient is shrimp shell powder from cleaned and dried shrimp waste. Other materials used are distilled water, Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4), hydrochloric acid (HCl), and potassium iodide (KI).

2.2 Methodology

2.2.1 Deproteination Method

Twenty-five grams of shrimp shells were dissolved in 100 mL of 1N NaOH in a beaker glass and heated at 65°C for 30 minutes using an electric stove. The solution was filtered until a precipitate was obtained. After that, the residue was washed using tap water until the pH was neutral. The residue was dried in an oven at 80°C for 45 minutes.

2.2.2 Demineralization Method

Put the deproteinated shrimp shells into a beaker, add 100 mL of 1N HCL, and then heat at 75°C for 30 minutes. The solution was filtered until a precipitate was obtained and then washed with tap water until the pH was neutral. Then, the residue was dried in an oven at 100°C and put in a desiccator. Next, the precipitate is weighed to a constant weight.

2.2.3 Test for the Presence of Chitin

10 mL of KI 1 N solution was added to the dry chitin product until it changed color to brown, then added H2SO4 1 N until it changed color from brown to red.

3. Results and Discussion

The process of making chitin was carried out in three methods: deproteination, demineralization, and testing for the presence of chitin. Chitin can be obtained from animal shells and crustaceans like shrimp. Shrimp shell contains 27.6% minerals, 34.9% protein, 18.1% chitin, and other components such as dissolved substances, fat, and digestible protein, about 19.4%. However, the amount of this content depends on the type of shrimp. Chitin can be processed into chitosan through a deacetylation process with polycationic properties to be used as a material for zinc-ion batteries [5].

The deproteination stage removes protein from chitin with the help of a strong base as a solvent [6]. This process aims to separate or release protein bonds from chitin. In the deproteination stage, the protein in the shrimp shell is soluble in the base so that the protein covalently bound to the chitin functional group will be separated. Using a NaOH solution with a high concentration and temperature is more effective in removing protein and causing the deacetylation process.

The demineralization stage aims to reduce the content of inorganic salts or $CaCO_3$ minerals and $Ca_3(PO_4)_2$ in shrimp shells [7]. Shrimp shell contains many minerals, characterized by the formation of CO_2 in the form of air bubbles when the HCl solution is mixed into the shrimp shell.

The reactions that occur during the demineralization process are as follows [7]:

$Ca_3(PO_4)_2(s) + 6HCl(aq) \rightarrow 3CaCl_2(aq) + 2H_3PO_4(aq)$

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

The final stage of making chitin from shrimp shells is testing for the presence of chitin. Qualitatively, the color reaction Van Wes link can detect chitin's presence. At this stage, chitin is reacted with I2 in KI, which gives a brown color, then if H is added2SO4 will change color to red. A color change from brown to reddish indicates a positive reaction to the presence of chitin [3].

In this experiment, 25 grams of shrimp shell powder were used, and the following result.

Table 1. were obtained

Trial	Dry Chitin Weight (grams)	Yield (%)	Gram Chitin / Gram Shrimp shell
1	9.56	38.16	0.38
2	2.44	9.76	0.1
3	3.05	12.2	0.12
4	11.68	46.72	0.47
average			0.27

From the data above, different weights of dry chitin were obtained due to differences in the type of shrimp shell used. The several factors that influence the process of making chitin are as follows [8]:

1. HCl concentration

The higher the concentration of HCl used, the faster the reaction rate will be. However, too much HCl can lead to increased acid waste in the environment.

2. Addition of NaOH
   The higher the concentration of NaOH, the higher the degree of deacetylation. However, using too much NaOH can cause an increase in alkaline waste in the environment.
3. Temperature
   The higher the temperature, the faster the reaction rate, but the yield is less because the compounds in the material are soluble in the solvent. However, temperatures that are too high can damage the material's structure.
4. Reaction Time
   The longer the reaction time, the lower the yield because the chitin compound is dissolved in the solvent.

The development of battery technology has become a significant focus on finding solutions for energy storage that are more efficient and environmentally friendly. One of the newest trends in this field is the zinc ion battery, also known as the zinc ion battery. This battery holds great promise in overcoming the limitations of current battery technology. However, the main challenge in developing these batteries is ensuring the availability of sustainable and environmentally friendly raw materials. This is where the potential of chitin, a compound found in the skeletons of insects and crustaceans, becomes relevant. Chitin is a natural polymer found in the skin/shells of insects, crustaceans, and fungi. It has a unique chemical structure and has the potential to be processed into raw materials in various applications, including zinc ion batteries. One of the significant advantages of chitin is its abundance. It is estimated that chitin is one of the most abundant biomasses on the planet, mainly due to its unlimited potential source of agricultural and industrial fishing waste.

In addition to its abundance, using chitin as a raw material for zinc ion batteries has significant environmental benefits. Chitin is obtained from the remaining waste of food production and fisheries, thus reducing the impact of this waste on the environment. In an effort towards sustainability, batteries that use chitin as a raw material can provide a more environmentally friendly alternative compared to conventional batteries, which often use raw materials that have the potential to damage the environment. Transforming chitin into zinc ion battery material involves several key steps. First, like in this study, chitin is extracted from its source, such as a shrimp shell or an insect's exoskeleton. The next step is to convert the chitin into compounds suitable for electrodes in batteries. This involves chemical processing to convert chitin into zinc-ion-soluble compounds that can be used as electrolytes in zinc-ion batteries [8].

Using chitin as a raw material in zinc ion batteries offers several technical advantages. Chitin can contribute to increased battery capacity, charging speed, and cycle stability. The chemical properties of chitin also allow it to reduce the risk of zinc dendritic damage, which can compromise battery performance and safety. Although the potential of chitin in zinc ion batteries is exciting, some challenges still need to be overcome. Extracting and processing chitin into suitable raw materials for batteries requires sophisticated technology and manageable production costs. In addition, further research is needed to gain a deeper understanding of the interactions between chitin and battery systems. However, with the drive towards innovation and sustainable solutions, chitin utilization in zinc ion batteries has great potential to change the energy storage paradigm. Chitin-based zinc ion batteries can contribute to reducing dependence on conventional raw materials that harm the environment. With hard work, scientific collaboration, and suitable investments, this potential can be realized to shape a cleaner and more sustainable energy future [9],[10].

4. Conclusion

From the results of the research that has been done, it can be concluded as follows:

Shrimp waste can be converted into products with high selling value, such as materials for zinc ion batteries, through the deacetylation process of chitin into chitosan. Shrimp shell waste can be converted into chitin through deproteination and demineralization methods. Color change in Van Weslink qualitatively proves the presence of chitin. The average total production of chitin is 0.27 grams of chitin/gram of shrimp shell.

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Author Contributions

Abdillah Syah Putra, Irma Sulistina, Mutiara Febrianti, and Nuril Mina Apdhila were performing the laboratory experiments, manuscript drafting, and data analysis while Cornelius Satria Yudha was supervising and finalizing the manuscript.

References

[1].Damanti, R. R. (2022). Rilis Data Kelautan dan Perikanan Triwulan 2022. Kementrian Kelautan dan Perikanan Tahun 2022.

[2]. Agusta, I. (2021). Ekstraksi Kitosan dari Limbah Kulit Udang dengan Proses Deasetilasi. Journal of Chemical Engineering, 2(2).

[3].Sry Agustina, I. M. D. S. dan I. N. S. (2015). Isolasi Kitin, Karakterisasi, dan Sintesis Kitosandari Kulit Udang. Jurnal Kimia, 9(2).

[4]. Siang Tandi Gonggo, A. W. M. D. dan R. L. (2017). Pengaruh Kaolin Terhadap Membran Blend Kitosan Poli Vinil Alkohol-Litium Sebagai Membran Elektrolit Untuk Aplikasi Baterai Ion Litium. Jurnal Akademika Kimia, 6(1).

[5]. Maulana, S., & Fadli, A. (2017). Kinetika Reaksi Demineralisasi Isolasi Kitin dari Cangkang Ebi. In Jom Fteknik (Vol. 4, Issue 2).

[6].Kamal Akbar, M. (2021). Deproteinasi Kitin Cangkang Kerang Kijing (Pilsbryoconcha Exilis) dengan Enzim Papain.

[7]. Salmahaminati. (2022). Synthesis of Chitosan from Crab Shells Using Microwave Heating Method (Vol. 7, Issue 1).

[8].Wahyuni, W., Ridhay, A., & Nurakhirawati, N. (2016). Pengaruh Waktu Proses Deasetilasi Kitin dari Cangkang Bekicot (Achatina Fulica) Terhadap Derajat Deasetilasi. Kovalen, 2(1).

[9]E. L. Diego Ruiz, Veronica F Michel, Markus Niederberger, "Chitin Nanofibrils from Fungi for Hierarchical Gel Polymer Electrolytes Enabling Transient Zinc Ion Batteries with Stable Zn Electrodeposition," Small, vol. 2303394, pp. 1–15, 2023, doi: 10.1002/smll.202303394.

[10] C. Liu et al., "A Chemically Self-Charging Flexible Solid-State Zinc-Ion

Battery Based on VO2 Cathode and Polyacrylamide–Chitin Nanofiber Hydrogel Electrolyte," Adv. Energy Mater., vol. 11, no. 25, pp. 1–11, 2021, doi: 10.1002/aenm.202003902.

[11] H. Li, Z. Wei, Y. Xia, J. Han, and X. Li, "Chitosan derived carbon membranes as protective layers on zinc anodes for aqueous zinc batteries," Int. J. Miner. Metall. Mater., vol. 30, no. 4, pp. 621–629, 2023, doi: 10.1007/s12613-022-2525-1.