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Sustainable and Environment-Friendly Management of Shrimp Processing Waste through High-Quality Chitosan Production

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Abstract

The shrimp processing industry generates substantial waste, including shells, heads, and tails, which, if not properly managed, can contribute to significant environmental issues, such as pollution and disease transmission. This study explores the conversion of shrimp waste into chitosan, a valuable biopolymer with applications across multiple industries, by utilizing its chitin, protein, and mineral content. The extraction process involved demineralization with 1M HCl, deproteinization with 3.5% NaOH, and deacetylation with 60% NaOH. The resulting chitosan exhibited high quality, characterized by a crystal structure, white color, odorless powder form, 73.7% degree of deacetylation (DD), 64% yield, solubility in acetic acid, and water content of 1.5%. This research highlights an environmentally responsible approach to shrimp waste management, providing a method for repurposing waste into a high-value material that meets industry standards, supporting environmental sustainability and circular economy practices.

1. Introduction

The fishing industry, particularly shrimp farming and processing, is one of the fastest-growing sectors in many countries, including Indonesia. High levels of shrimp production, recorded at 861,336 tons in 2020 according to the Central Bureau of Statistics [1], result in a substantial amount of byproduct and waste. This waste can significantly harm the environment [2].

Shrimp waste can lead to significant environmental issues if not properly managed, including water pollution and unpleasant odors from organic decomposition. It poses various environmental hazards, such as contributing to waste accumulation, emitting odors, and becoming a source of disease [3, 4]. Addressing these challenges requires sustainable waste management solutions that transform waste into valuable resources, supporting a shift towards a circular economy and promoting environmentally friendly practices [5, 6].

Chitosan is a chitin derivative compound with an active amine substance that is non-toxic and can be implemented in various ways. Utilizing shrimp waste to produce value-added products not only offers solutions to environmental problems but also creates new economic opportunities, especially in the fields of cosmetics, food, medicine, and agriculture [7, 8]. Chitosan can be obtained by removing acetyl in chitin through the deacetylation process. The loss of acetyl will be proportional to the quality of the chitosan obtained [9–15].

Processing shrimp waste into chitosan offers extensive potential across multiple industries. In cosmetics, chitosan serves as a natural moisturizer, anti-aging ingredient, and skin healing agent [16, 17]. It is also used in biosensors [18, 19] and pharmaceuticals [5, 20]. In waste treatment, chitosan absorbs heavy metals and color pollutants. In healthcare, it is utilized in wound care, immunology, and as an anticoagulant.

Moreover, shrimp waste can be repurposed to produce animal feed and bioplastics, which are increasingly in demand as eco-friendly material alternatives [21, 22]. This approach shifts the perception of waste from a burden to a valuable resource with high economic potential. Processing shrimp shell waste into chitosan generates products with market value and contributes to environmental sustainability by reducing pollution [23].

This study aims to explore the efficient extraction of chitosan from shrimp waste and assess its potential applications across various industries. Specifically, it focuses on refining the extraction process to enhance chitosan quality, ensuring that the derived product meets the standards required for applications in cosmetics, pharmaceuticals, waste treatment, and other sectors. By examining the methods for obtaining high-quality chitosan from locally sourced shrimp waste, this study seeks to contribute to sustainable waste management solutions within the shrimp industry and establish a feasible approach for converting byproducts into valuable materials.

The findings of this research contribute to sustainable waste management in the shrimp industry by demonstrating how shrimp waste can be repurposed into a high-value product. This study addresses environmental issues associated with shrimp waste disposal while providing an effective method for producing chitosan that aligns with sustainable practices. The outcomes of this research are intended to inform and benefit shrimp processors, waste management sectors, and industries seeking eco-friendly material solutions, thereby promoting a circular economy and supporting the development of green technologies.

2. Materials and Methods

2.1. Materials

The primary materials used in this study included aquades (distilled water), shrimp shells sourced from Bengkulu, Indonesia, hydrochloric acid (HCl p.a.), sodium hydroxide (NaOH p.a.), and acetic acid (CH_3COOH p.a.). All chemicals used were of analytical grade, ensuring accuracy and consistency throughout the deacetylation process for chitosan extraction. The selection of high-purity reagents was essential to producing high-quality chitosan and optimizing its properties for applications across various industries. The shrimp shells provided a local and sustainable source of chitin, further aligning with the study's focus on environmental sustainability and resource utilization.

2.2. Chitosan Extraction and Characterization Procedures

2.2.1 Cleaning of Shrimp Waste

The initial step in the chitosan production process involves collecting shrimp shells or waste, including parts such as shells, heads, and tails. Once gathered, the shrimp waste is thoroughly washed with clean water to remove any residual dirt, meat, or fat. This cleaning process is crucial to ensure that the raw materials are free from contaminants that might affect the production process. After washing, the shrimp shell waste is dried in an oven at 110 °C for one hour and then stored in a desiccator. The dried shells are ground and sieved to a fine powder with a particle size of 100 mesh.

2.2.2 Demineralization

For demineralization, 200 grams of the shrimp shell powder are mixed with a 1 M HCl solution at a ratio of 1:15 (w/v). This mixture is heated at 60-70 °C for four hours, followed by washing with distilled water (aquades) until the pH becomes neutral. Afterward, the demineralized shrimp shell powder is dried in an oven at 80 °C for 24 hours and then cooled in a desiccator. The resulting powder is analyzed using FTIR to determine its chitin content.

2.2.3 Deproteinization

The demineralized shrimp shell powder is then subjected to deproteinization. It is combined with a 3.5% NaOH solution in a 1:10 (w/v) ratio of solvent to sample. This mixture is heated at 60 °C for four hours while being stirred at a speed of 50 rpm. After heating, the powder is washed with aquades until it reaches a neutral pH, dried in an oven at 80 °C for 24 hours, and finally cooled in a desiccator.

2.2.4 Deacetylation

In the deacetylation step, the demineralized shrimp shell powder is treated with 60% NaOH at a ratio of 1:20 (w/v). The mixture is stirred and heated in an oil bath at 110 °C for four hours. The resulting product is then washed with aquades until it reaches a neutral pH, dried in an oven at 80 °C for 24 hours, and cooled in a desiccator. The final shrimp shell powder is analyzed using FTIR to confirm chitosan content.

2.2.5 Chitosan Yield

The chitosan yield is calculated as the percentage of chitosan weight produced relative to the initial weight of the shrimp waste.

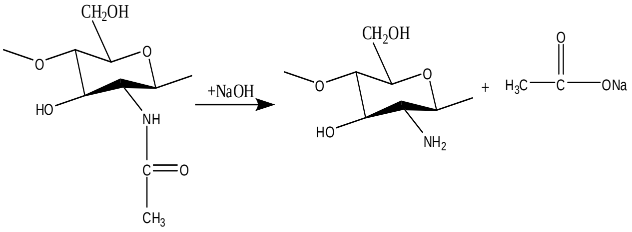

Figure 1. Reaction for deacetylation.

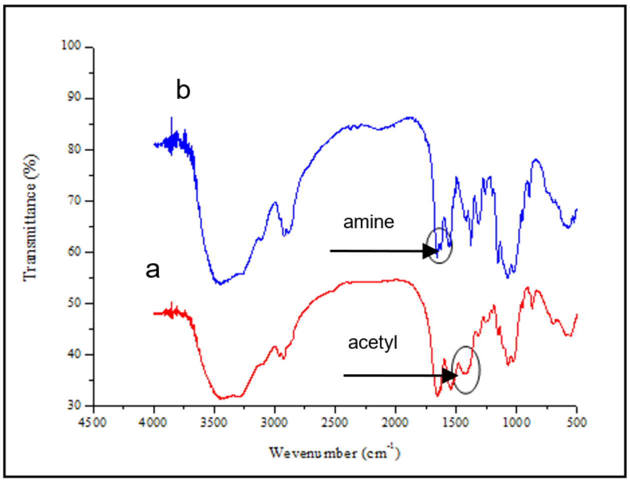

Figure 2. FTIR results of chitin (a) and chitosan (b).

2.2.6 Water Content

To determine the water content, 0.5 grams of chitosan is weighed into a pre-weighed porcelain cup and placed in an oven at 100 °C for one hour. The sample is then cooled in a desiccator for 30 minutes and weighed. This heating and cooling process is repeated until a constant weight is achieved.

2.2.7 Chitosan Solubility

Chitosan solubility serves as a quality parameter, with higher solubility indicating better quality. In this analysis, 1 gram of chitosan is dissolved in 2% glacial acetic acid at a ratio of 1:100 (g/ml), and the solubility is assessed to establish the standard quality of the produced chitosan.

3. Results and Discussion

Shrimp shells contain valuable compounds, including chitin, proteins, minerals, and pigments, that can be transformed into high-quality products. Processing shrimp shell waste into chitosan involves several key steps: demineralization, deproteinization, and deacetylation. The isolation of chitin begins with demineralization, where a 1 M HCl solution is used to remove inorganic salts or mineral content present in the chitin. The salts found in shrimp shells include calcium, magnesium, phosphorus, iron, manganese, potassium, copper, sodium, zinc, and sulfur. Of these, calcium carbonate ($CaCO_3$) is the most abundant mineral.

During demineralization, the minerals in the sample react with HCl, leading to the separation of minerals from the shrimp shells. This mineral separation is evidenced by the release of CO_2 gas, visible as air bubbles when HCl is added to the sample. To prevent overflow, HCl is added gradually, allowing for a controlled gas release. The reaction that occurs during demineralization is as: $CaCO_3(s) + 2HCl(l) \rightarrow CaCl_2(s) + H_2O(l) + CO_2(g)\uparrow$.

Shrimp shells obtained from the demineralization stage proceed to the deproteinization stage, where a 3.5% NaOH solution separates or releases protein bonds from chitin. In this step, the proteins within the shrimp shells dissolve in the alkaline solution, effectively breaking the covalent bonds between the proteins and the chitin functional groups. Following deproteinization, the next crucial step is deacetylation, a key phase in converting chitin into chitosan.

Deacetylation involves the removal of acetyl groups (-$COCH_3$) from chitin, the primary polysaccharide found in shrimp and other crustacean shells, producing chitosan—a valuable derivative of chitin. This transformation is essential because deacetylation makes chitosan more reactive and suitable for various commercial applications, thereby enhancing its market value. In an alkaline environment, the deacetylation process facilitates the formation of additional amine groups. High concentrations of NaOH provide abundant -OH groups, which react with the -$COCH_3$ groups, leading to an increased number of amine groups and, consequently, a higher degree of deacetylation. The chemical reaction for the deacetylation process is illustrated in Figure 1.

One important parameter in the deacetylation process is the degree of deacetylation (DD), which refers to the percentage of acetyl groups removed from chitin. This degree of deacetylation is very important as it affects the physical and chemical properties of chitosan, including solubility, mechanical strength, and biological activity. Chitosan with high DD (above 70%): More soluble in acids and often used for medical, pharmaceutical, and biotechnology applications. Chitosan with low DD (below 70%): The chitosan produced in this study had a degree of deacetylation of 73.7%. The functional groups in chitin and chitosan were analyzed by FTIR [24, 25]. This aims to determine the changes and differences in functional groups between chitin and chitosan. The change of the acetyl functional group into an amine is an indicator of the success of the chitosan synthesis process [26]. The results of the FTIR analysis can be seen in Figure 2.

The results of the FTIR analysis showed that there was a change in several functional groups in chitin. After the

Table 1. Yield of chitin and chitosan.

No	Parameter	Result
1	Shrimp shell weight before demineralization	200 g
2	Shrimp shell weight after demineralization	94 g
3	Shrimp shell weight after deproteinization (chitin)	72 g
4	Yield of chitin	36%
5	Chitin weight for chitosan synthesis	70 g
6	Chitosan result synthesis	45 g
7	Yield of chitosan	64%

Table 2. Characteristic of chitosan.

No	Parameter	Chitosan International Standard	Chitosan Produced
1	Shape	Crystal	Crystal
2	Smell	No smell	No smell
3	Color	White	White
4	DD	≥70%	73.7%
5	Texture	Powder	Powder
6	Solubility in acetic acid	soluble	soluble
7	Water content	<10%	1.5%

deacetylation process, the C=O group at a wavelength of 1680-1660 cm^{-1} was lost. This indicates that acetyl is lost in the synthesized chitosan. There is a vibration of the NH_2 group which indicates that the acetyl group is released and an amine group (NH_2) is formed [20, 26].

The results of this study showed a chitin yield of 36%. This yield is significantly higher than the 9.54% yield reported by Ernawati [27], indicating a more effective extraction process in this study. The higher percentage yield demonstrates the efficiency of chitin extraction from the raw shrimp shell material. The yield results from this process are presented in Table 1.

This study achieved a chitosan yield of 64%, which is notably higher than the 26.33% yield reported by Sinaga [28], who used 50% NaOH in the deacetylation process. The higher yield in this study can be attributed to the use of a higher NaOH concentration (60%), which accelerates the reaction, increasing the likelihood of collisions between the chitin and the strong base. As a result, a larger amount of chitin is successfully converted into chitosan. This percentage yield reflects the effectiveness of the chitosan extraction process from chitin.

The chitosan produced in this study meets international quality standards, with a degree of deacetylation (DD) of 73.7%, a white color, no odor, and low water content. The water content in chitosan is influenced by factors such as drying efficiency, drying duration, the quantity of chitosan being dried, and the surface area exposed during drying. Chitosan's solubility in glacial acetic acid serves as a key parameter for assessing its quality. Higher solubility in 2% glacial acetic acid (1g/100ml) indicates higher quality chitosan. The chitosan produced in this study exhibits complete solubility in 2% glacial acetic acid, confirming its high quality as reflected by international standards, as shown in Table 2 [29].

This study effectively demonstrates the feasibility of extracting chitosan from shrimp waste, yet certain limitations must be acknowledged. The process's reliance on high concentrations of NaOH and HCl, while effective, raises environmental and safety concerns due to the potential for chemical waste. Additionally, while FTIR analysis was used to confirm chitosan quality, more in-depth chemical characterization techniques like X-ray diffraction or thermogravimetric analysis could provide further insights into chitosan's structural properties and thermal stability. These additional analyses could support a more comprehensive understanding of chitosan's suitability across diverse applications. Finally, scaling up the process to industrial levels may present challenges, as maintaining consistent chitosan quality and yield could be affected by variations in shrimp shell composition across different sources and batches.

Future research should focus on optimizing environmentally friendly methods for chitosan extraction to minimize chemical usage and waste. Exploring alternative methods, such as enzymatic or biotechnological processes, could provide sustainable options for large-scale production. Additionally, future studies could investigate the effects of various shrimp sources, seasons, and regional differences on chitosan yield and quality to develop standardized practices for commercial application. Expanding the range of applications through tailored chemical modifications of chitosan could also be beneficial, particularly for high-demand sectors like biodegradable packaging and advanced medical therapies. Overall, refining extraction processes and broadening application testing will be essential for fully capitalizing on the environmental and economic potential of chitosan derived from shrimp waste.

4. Conclusions

Processing shrimp shell waste into high-quality chitosan presents both challenges and opportunities. Variability in raw materials affects yield based on shrimp type and handling conditions while scaling up production from laboratory to industry requires substantial investment and advanced technology. Despite these hurdles, rising market demand, improved extraction methods, and supportive policies for sustainable waste management create a positive outlook for the industry. The chitosan produced in this study exhibits high quality, with desirable properties such as a crystalline structure, white and odorless powder form, 73.7% degree of deacetylation, 64% yield, solubility in acetic acid, and low water content (1.5%). These characteristics make it suitable for applications in cosmetics, pharmaceuticals, waste treatment, and beyond. Ultimately, this study underscores the potential of shrimp waste as a valuable resource, supporting eco-friendly practices, contributing to a circular economy, and promoting green technology development in the shrimp industry.

Conceptualization, Z.Z. and W.A.H.M.; methodology, Z.Z.; software, Z.Z.; validation, Z.Z., W.A.H.M. and K.K.; formal analysis, Z.Z.; investigation, Z.Z.; resources, Z.Z.; data curation, Z.Z.; writing—original draft preparation, Z.Z.; writing—review and editing, Z.Z.; visualization, Z.Z.; supervision, Z.Z.; project administration, Z.Z.; funding acquisition, W.A.H.M. All authors have read and agreed to the published version of the manuscript.

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