EFFECT OF MICROWAVE IRRADIATION TIME TO DEACETYLATION PROCESS OF CHITIN FROM SHRIMP SHELLS

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Abstract

Microwaves have been used in various organic synthesis applications. The use of microwaves provides many advantages, including relatively short start-up and heating times, energy efficiency and process costs, easy and precise process control, selective heating, better final product quality, and improved dry material quality. Microwaves were used in this study to convert chitin into chitosan and to determine the effect of deacetylation time on the degree of deacetylation of chitosan, which was in accordance with the Indonesian National Standard (SNI 7949:2013). The chitin deacetylation process was carried out by varying the heating time to 5, 7, 11, and 15 minutes with a power of 350 W. Two grams of chitin were mixed with 40 mL of 70% NaOH solution in a beaker. The mixture was put in a microwave at a constant temperature of 70 °C. Chitosan was washed until neutral and then dried in an oven. The degree of deacetylation (DD) was analyzed using Fourier Transform Infrared (FTIR) spectroscopy. The results showed that A deacetylation degree of 79.96% was achieved at a reaction time of 15 min. The water content of chitosan was determined to be 9.15%.

***Keywords**: chitin, chitosan, microwave*

Introduction

Microwave technology has been widely used in various applications in food and chemical industries. Microwaves can be used as a power source to heat and dry materials, and catalyze chemical reactions in the manufacture of industrial and agricultural materials (Liu et al., 2005). The use of microwaves provides many advantages, including relatively short startup and heating times, energy efficiency and process costs, easy and precise process supervision, selective heating, better quality of the final product, and improved dry matter (Sumnu, 2001). Microwaves are often used as external forces to accelerate the chemical reactions. These are called "microwave-assisted reactions." Chemical methods have been widely used to produce chitosan. A strong alkaline solution with a high concentration, high temperature, and long duration is necessary for the procedure. Technological innovation is required for a production process to run quickly, optimally, and efficiently. Microwaves were the technological advancements used in this investigation to deacetylate chitin derived from shrimp shell waste. Compared to traditional heaters, microwave radiation can speed up the reaction rate 10–100 times. Microwaves should accelerate the reaction time and increase deacetylation levels.

Arifin et al. studied the production of chitosan from shrimp shell waste, and their results were the best for chitosan, with the highest deacetylation degree value of 85.32% at a NaOH concentration of 70% and a reaction period of 15 min. SNI 7949:2013 was used to set chitosan quality criteria, which included testing for a minimum deacetylation degree of 75% (Septiwi, 2014). The objective of this study was to develop a method for producing chitin that satisfies the minimal standards of SNI 7949:2013 using less microwave power.

Therefore, the degree of deacetylation obtained satisfied the chitosan quality standards. This study can be enhanced based on the available references. The issue in this study was that not all chitin was converted into chitosan through deacetylation. The degree of deacetylation (DD) of > 90% indicates that chitosan is perfectly deacetylated (Srijianto, 2003). The low level of deacetylation in the research findings was due to several variables, including temperature, habitat type, and shrimp management. By studying the impact of microwaves on the reaction time during the chitin deacetylation process when producing chitosan from shrimp shell waste, Arifin et al. improved the degree of deacetylation. The advantages of microwaves include faster startup times, quicker heating, energy efficiency, process costs, simple and accurate process supervision, selective heating, and superior product quality (Mojarrad *et al.*, 2007).

Agustina S, et al. studied the production of chitosan from shrimp shell waste and obtained the best results for chitosan, with the highest deacetylation degree value of 84.85% at a NaOH concentration of 60% via demineralization and deproteination. The degree of deacetylation that results fit with the SNI 7949:2013's Quality Standards. The resultant chitosan contains only 1.55% water. Because the generated chitosan already has a very high moisture content, it does not alter the resistance of mycoorganisms to chitosan. The flaw of this study is that none of the chitin obtained was converted into chitosan through deacetylation. If DD > 90%, chitosan was considered to have undergone perfect deacetylation (Srijianto, 2003). The manner in which the mixture was agitated and how heated it contributed to the low level of deacetylation found in this study.

Zaeni et al. studied the production of chitosan from shrimp shell waste and obtained the best results for chitosan with the highest deacetylation degree value of 62.72 percent at a NaOH concentration of 50 percent via demineralization and deproteination. Based on Quality Standards, the degree of deacetylation produced did not meet these requirements (SNI 7949:2013). The ideal deacetylation reaction operating condition was 15 min with 450 watts of microwave power. Thus, the degree of deacetylation obtained cannot be considered to have met chitosan quality standards.

The objective of this study was to determine the impact of microwave irradiation time on the degree of chitosan deacetylation to fulfill the Indonesian National Standard requirements (SNI 7949:2013).

Research Methods

The primary ingredients used in this study were shrimp shells obtained from traditional markets, NaOH 70%, and aquades (Arifin and Effensi, 2017). The equipment used was a microwave, blender, beaker cup (50, 100, and 250 mL), hot plate, litmus paper, filter, spray bottle, drip pipette, 110 °C oven, 50 mL volume pipette, watch glass, bulp, spatula, stirring rod, plastic, and filter paper. This study used microwave times of 5, 7, 11, and 15 min. The variables analyzed in this study were the degree of deacetylation and water content.

According to Zaeni et al., chitin must be prepared first. The blended chitin was sieved through a -10+20 mesh of size. Chitin (2 g) was combined with 70% NaOH solution (Arifin and Effensi, 2017). Then, the mixture was placed in a microwave at a power of 350 times variation for (5, 7, 11, and 15 minutes).

Then it was dried for three hours at 110°C after being washed with aquades at 70°C to a neutral pH. The degree of deacetylation was then measured by using FTIR instrument, and the amount of water in the chitosan was determined using an oven.

Results and Discussion

This study aimed to determine the effect of microwave deacetylation time on the degree of deacetylation of chitosan to conform to the Indonesian National Standard (SNI 7949:2013) (Table 1). A microwave-assisted deacetylation method with time variations of 5, 7, 11, and 15 min and power of 350 watts was used in this experiment (Table 2). The raw material used for the production of chitosan was -10+20 mesh of shrimp shells (Table 3).

Table 1. Deacetylation degree analysis results

Sample	Deacetylation time (minutes)	Degree of deacetylation
1	5	79.50
2	7	79.80
3	11	79.85
4	15	79.96

Table 2. Chitosan FTIR analysis results

Functional Clusters	Wavenumber (cm^{-1})	Transmitant (%)
OH	3368.28	104.5
N-H	1647.09	98.5
C-O-C	1021.84	82.5
C-H Stretching	2325.67	102
C-H bending	1416.38	90

Table 3. Chitosan analysis results based on SNI

Parameter	Standard	Research
Particle Size	Flakes to powder	Flakes
Moisture Content (%)	≤10	9.15
Degree of Deacetylation	≥70	79.96
Solubility in Acetic Acid 1%	Soluble	Soluble

The use of microwaves changes the direction of rotation of the water molecules. Similar to a compass needle, water molecules are polar, with a positively charged side and a negatively charged pole. If one or both poles are in a strong electric field owing to the presence of microwaves, a repulsive force will exist, which causes the water molecules to spin. As a result of spinning, heat and friction develop (Lee, 2000). This research uses heat.

NaOH (70%) was used for the deacetylation. NaOH was used to hydrolyze chitin to chitosan. During deacetylation, a substituted chitin acetyl group (acetamide group) breaks the bonds between carbon and nitrogen to create an amine group. Figure 1 shows how the NaOH hydrolyzed chitin.

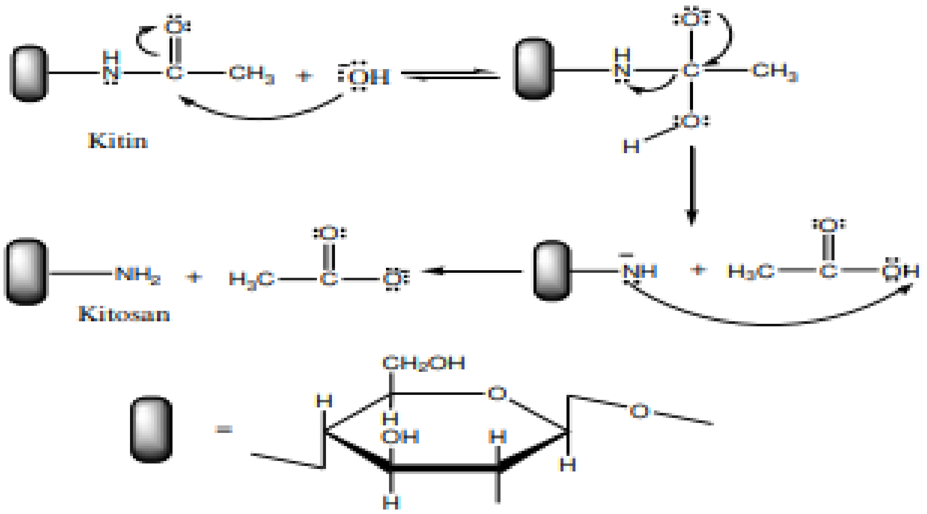

Figure 1. FTIR analysis chart

The characterization of chitin and chitosan carried out in this study included the characterization of functional groups in chitin and chitosan by infrared spectroscopy and determination of the degree of deacetylation. The infrared spectra of chitosan are shown in Figure 2. The interpretation of the vibrational bands of the chitosan functional groups is shown in Table 2.

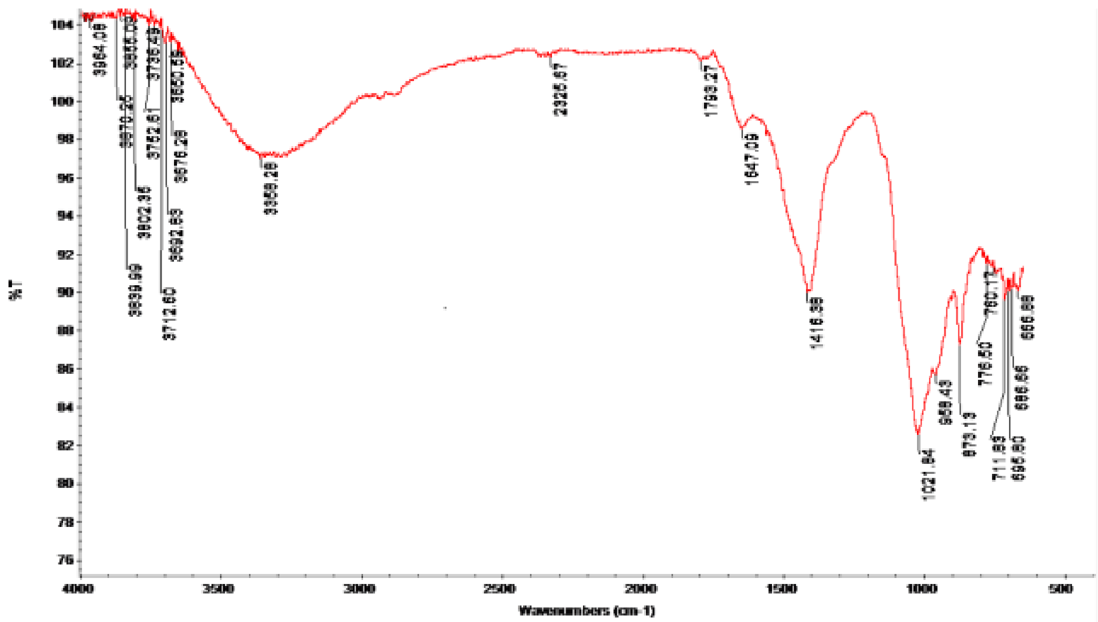

Figure 2. Result of FTIR analysis of chitosan samples

The FTIR spectra for shrimp shell chitin revealed an absorption pattern at a wavelength of 3368.28 cm^{-1}, indicating a broadened OH vibration, as can be seen from the chitosan infrared spectra in Figure 2. Another absorption occurred at 2325.67 cm^{-1} in aliphatic C-H assistance. As for the bending vibration, N-H appears at wave number 1647.09 cm^{-1}. Because chitin hydroxide contains a single bond, C=O, it absorbs in the range of 1021.84 cm^{-1} in the shell of the shrimp C-O-C vibration, which causes the chitin ring to contain several peaks.

In the process of making chitosan, there are some chitins that have not turned into chitosan, so that the chitosan obtained is not purely a chitosan compound, but has been mixed with chitin. This can be determined from the degree of deacetylation of chitosan by using the *base line method*. This method is based on a comparison of the absorbance values of the absorption band of the infrared spectrum at wavenumbers of 1655 cm^{-1} and 3450 cm^{-1}. Thus, the chitin deacetylation process with a NaOH concentration of 70% and a time of 15 min yielded a chitosan deacetylation degree of 79.96.

To determine the effect of deacetylation time, time variations of 3–15 min were performed using 70% NaOH. At 70 °C, the deacetylation temperature was selected. The selection of 70 °C was based on many results from previous research (Sakti, 2011; Dono, 2012; Dumais, 2013). Time variations of less than 30 min were chosen to assess the performance of microwave technology in comparison with other methods, such as ultrasonics and conventional methods. The deacetylation reaction time can be reduced owing to the rate and efficiency of heat transfer generated by microwaves. The effect of the microwave radiation time on the degree of deacetylation is shown in Figure 3.

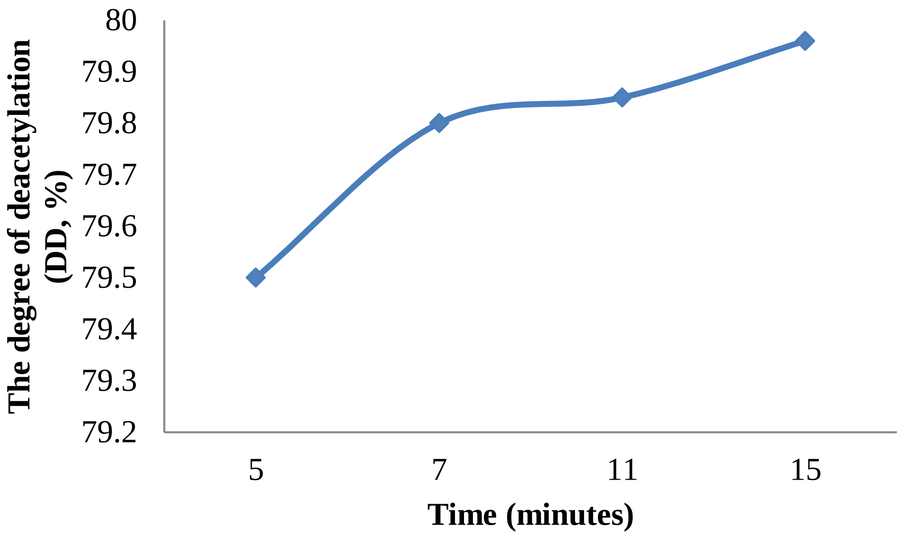

Figure 3. Radiation time effect on degree of deacetylation

Increased response time influenced the degree of deacetylation. In the reaction time span of 3 min to 15 min, there was an increase in the degree of deacetylation, and there was a decrease in the degree of deacetylation at the various powers used. The degree of deacetylation attained at 350 watts of steadily increased as the reaction time increased. At a response time of 5–7 minutes, there is a 0.3% rise in the degree of deacetylation. When the reaction took 7–11 min, there was an increase of 0.05%, and when it took 11–15 min, there was an increase of 0.11%. According to estimates, the degree of deacetylation tends to decrease with increasing reaction time. An increased response time and power usage can contribute to a decline in deacetylation levels. An increase in reaction time will have an impact on the degree of deacetylation as well as the molecular weight of the chitosan generated, resulting in low-viscosity chitosan (Sahu et al., 2009).

The microwave power and reaction time are two interacting factors. Because this reduces the possibility of thermal degradation, the combination of low power and long reaction time is a wise choice. (Langa *et al.*, 1996) . The longer the reaction time, the more microwave radiation is emitted; thus, the radiation absorbed by the reaction components is greater. The orientation of the reaction component to a large magnetic field results in the conversion of kinetic energy into substantial thermal energy, thereby increasing the random motion of the molecules. Molecule collisions increase because of the random motion of the molecules. The energy and speed of liquid molecules are determined by their specific temperatures. The chemicals in the reaction mixture evaporate much more quickly as a result of the effect of the temperature increase on the energy of the gas molecules. The microwaves used in this experiment did not have a condenser, allowing the steam produced by the material to leave the reactor (Ajavakom *et al.*, 2012).

Conclusions

According to previous research that has been conducted, 15 min at 350 watts of microwave power is the ideal deacetylation reaction operating condition as a time function. The chitosan had a moisture level of 9.15% and a deacetylation level of 79.96%.

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