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Utilization Of Nano Chitosan From Crab Shells (*Portunus Pelagicus*) As Bioadsorbent To Reduce Ion Of Heavy Metals Of Iron (Fe) From Water

Dheani Nur Ahadya Syifa Chaerunissa1 and Rozi2

1Faculty of Fisheries and Marine, Airlangga University, Surabaya, Indonesia
2Faculty of Fisheries and Marine, Airlangga University, Surabaya, Indonesia

Abstract: *The demand for Portunus pelagicus) increases every year, this has encouraged an increase in crab production in both the capture and aquaculture sectors. Indonesia is number four in the country that exports the most pasteurized crab meat. From 2019 to 2020, export volume increased by 13.25%. Increasing exports in the form of pasteurized crab meat has the potential to increase waste. Waste in waters can come from industrial, household, agricultural and aquaculture activities. Waste has the potential to pollute the environment through direct discharge into the environment. This research was carried out in April-October 2023. It was carried out at the Analytical Chemistry Laboratory of the Faculty of Science and Technology, the Biotechnology Laboratory of the Faculty of Fisheries and Marine Affairs, the Multipurpose-3 Laboratory for Analysis of Materials/Materials/Products of the Faculty of Pharmacy, and the Engineering and Engineering Life Sciences Institute, Airlangga University. The method used in this research was an experimental method. The research design used was a Completely Randomized Design (CRD) using 6 types of treatment, namely negative control with 100 mg/L sterile distilled water, positive control with 100 mg/L chitosan, and the addition of nanochitosan as bioadsorbent with doses of 25 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L and 3 repetitions for each treatment. The research parameters observed in this study were the bioadsorbent dosage of crab shell nanochitosan (Portunus pelagicus), nanochitosan particle size, and the content of the heavy metal iron (Fe). The data obtained is data on the reduction in levels of the heavy metal ion iron (Fe), then analyzed using statistical tests. The statistical test used in this research is Analysis of Variance (ANOVA) and followed by the Duncan 95% test if there are significant differences in the treatments. Based on the research, nanochitosan derived from crab shells shows that the effectiveness of nanochitosan from crab shell as a bioadsorbent is between 68.41% ± 0.46 and 82.75% ± 0.2. The optimum dosage of nanochitosan from crab shell as a bioadsorbent is at 400 mg/L.*

Keywords—nanochitosan; blue swimming crab; gelasi ionic; wastewater; iron

1. INTRODUCTION

The demand for crab (Portunus pelagicus) increases every year, this has encouraged an increase in crab production both in the fishing and cultivation sectors. According to Farihin et al. (2015), crab shells contain chitin which can be processed into chitosan, which ranges from 40% -60%. Based on data from the Ministry of Maritime Affairs and Fisheries. (2020), Indonesia is number four in the country that exports the most pasteurized crab meat. In 2019 to 2020, export volume increased by 13.25%. Increasing exports in the form of pasteurized crab meat has the potential to increase waste (Natalia et al., 2021).

Waste in waters can come from industrial, household, agricultural and aquaculture activities. Waste has the potential to pollute the environment through direct discharge into the environment. According to statistical data from the Ministry of Environment and Forestry in 2020, 13 Indonesian provinces experienced Fe metal water pollution above the threshold (>0.3 mg/L). Iron (Fe) is a type of heavy metal that is essential in aquaculture activities. Fe metal in aquaculture activities usually comes from the soil of cultivation ponds, the feed used, metabolic waste from fish bodies, and fertilizers used in preparing cultivation ponds (Suriawan et al., 2019). Fe metal can cause biomagnification in the food chain so that it accumulates and harms other organisms and even humans, causing a destructive impact on biodiversity and fisheries productivity in nature, so that effective water waste management efforts are needed (Sutrisno et al., 2016; Emenike et al., 2021).

According to research conducted by Sisyanreswaei, et al. (2014) and Sasidhran et al. (2021), processing waste with the chemicals lime, alum and iron salts is toxic to aquatic organisms and humans and has a negative impact on the environment, so it is necessary to process waste that is environmentally friendly and safe for aquaculture organisms by using natural materials such as chitosan. Chitosan is chitin that has undergone a deacetylation process leaving acetyl groups with a content of no more than 40-45%. chitosan has low adsorption power, this has encouraged several researchers to modify chitosan physically or chemically into the form of nanoparticles (nanokitosan) to increase its adsorption power (Benettayeb et al., 2023). Nanochitosan in processing heavy metals was studied by Ali et al. (2018) by applying nanochitosan from shrimp shells to reduce levels of heavy metals such as Fe (II), with an optimum dose it can reduce the concentration of Fe (II) metal by 99.8%.

Nanochitosan has better and more stable absorption capabilities than chitosan, because it has a small size and a

more specific surface. Nanochitosan is environmentally friendly, so it can be used in wastewater treatment because it is chemically inert, and its shape is resistant to various complex conditions. Nanochitosan can be an alternative for processing heavy metal waste which is non-toxic, antimicrobial, biodegradable and biocompatibility (Kurniawidi et al., 2022; Benettayeb et al., 2023).

Based on the description above, this research utilizes the chitin content into nanochitosan from crab shells using the ionic glassic method as a bioadsorbent to reduce levels of the heavy metal iron (Fe). Research related to the use of chitosan has been widely carried out, however the use of chitosan in the form of nanoparticles from crab shells in reducing levels of the heavy metal iron (Fe) is still rarely carried out. So this research was carried out with the aim of determining the effectiveness of nanochitosan from crab shells as a bioadsorbent in reducing levels of the heavy metal ion iron (Fe) in water.

2. METHODOLOGY

2.1 Time and Place

This research was carried out in April-October 2023. The process of making chitosan was carried out at the Analytical Chemistry Laboratory, Faculty of Science and Technology, Airlangga University. The process of making nanochitosan and testing for heavy metals was carried out at the Biotechnology Laboratory, Faculty of Fisheries and Marine Affairs, Airlangga University. FTIR Test, PSA Test, and AAS Test were carried out at the Multipurpose-3 Material/Material/Product Analysis Laboratory, Faculty of Pharmacy, Airlangga University. The SEM test was carried out at the Institute of Biological Sciences and Engineering, Airlangga University.

2.2 Equipments and Materials

Equipment used in this research includes heater, desiccator, oven, glass beaker, glass stirrer, measuring cup, measuring pipette, bulb, thermometer, pH meter, porcelain cup, test tube, Erlenmeyer, magnetic stirrer, Buchner funnel, grinder machine, flask measuring glass, beaker, Particle size analyzer (PSA), Atomic Adsorption Spectmetry (AAS), analytical balance, and Fourier Transform Infrared (FTIR).
The material used to make nanochitosan is crab shells (CV. Colony Wallet, Surabaya). The chemicals used were 3.5% and 50% NaOH (Merck, Germany), 2M HCl (Rofa, RLC2.0068.0500, Indonesia), 1.5% acetic acid (Merck, Germany), Whatman filter paper no. 42, distilled water, and sodium tripolyphosphate (NaTPP) 0.1% (Merck, Germany), and FeSO4 salt. H2O 1000 ppm (Merck, Indonesia), and tween 80%.

2.3 Procedures

2.3.1 Preparation

Crab shell waste is cleaned from remaining meat attached and soaked in 2% NaOH solution 1:20 (w/v) for ± 12 hours to remove remaining meat or dirt attached to the crab shells, then washed with running water until the pH is neutral and checked. using universal pH paper. The crab shells are dried in the sun at a temperature of 37–40˚C until the shells are dry for 12 hours. The dry crab shells are ground using a grinder machine, then 1000 grams are weighed as the initial weight of the crab shell raw material before entering the chitosan manufacturing process stage (Ali et al., 2018).

2.3.2 Preparation of 3.5% NaOH solution (w/v)

3.5 g of 98% NaOH was weighed and dissolved in distilled water in a 50 mL beaker. The solution was then transferred into a 100 mL volumetric flask and diluted by adding distilled water to the mark. The solution in the volumetric flask is then homogenized.

2.3.3 Preparation of 2M HCl solution (v/v)

19.10 mL of the 32% HCl solution was pipetted and put into a 100 mL volumetric flask. The solution was diluted by adding distilled water to the limit mark and then homogenized.

2.3.4 Preparation of 50% NaOH solution

50 grams of 98% NaOH was weighed and then dissolved in distilled water in a 50 mL beaker. The solution was then transferred into a 100 mL volumetric flask and diluted by adding distilled water to the mark. The solution in the volumetric flask is then homogenized.

2.3.5 Making chitosan from crab shell chitin

The process of making chitosan from crab shells consists of demineralization, deproteination, depigmentation and deacetylation stages. Demineralization was carried out using 16.6 ml of 32% HCl, which was diluted with distilled water in a volumetric flask to the limit mark, then the crushed crab shells were put into a 1000 ml beaker to the extent of 80 grams. The HCl solution was mixed in a glass beaker and stirred with a magnetic stirrer at a temperature of 65ºC for 2 hours at a speed of 120 rpm, to maximize the process of releasing mineral substances that were still present in the crab shells. The crab shells have been soaked in HCl solution, then neutralized with running water to remove the acidic properties of the crab shells by measuring the pH of the washing water until it is neutral using universal pH paper, followed by drying in the oven at 50°C for 12 hours or until dry (Natalia et al., 2021).

Deproteinization was carried out using 5% NaOH, which was made by mixing 5 grams of 100% NaOH crystals in 100 ml distilled water, then homogenized with a magnetic stirrer at a temperature of 75ºC for 2 hours at a speed of 200 rpm, followed by the neutralization process using running water. Neutralization is carried out to remove the alkaline properties that are still present in the crab shells until the pH is neutral. The crab shells resulting from the deproteination process have a neutral pH, then are oven at 50°C for 12 hours or until dry (crude chitin). Dried crab shells that have gone through the deproteination and demineralization stages are called chitin (Natalia et al., 2021).

Depigmentation is carried out using acetone. The ratio between acetone and chitin is 1:10, the resulting precipitate is then washed with distilled water until the pH is neutral. The precipitate was filtered and dried in an oven at a temperature of 50°C. The chitin obtained then goes into the deacetylation

stage, using 50% NaOH which is made by dissolving 50 grams of 100% NaOH crystals in 100 ml of distilled water. The deacetylation stage is completed, followed by a neutralization process with distilled water until the pH is neutral using universal pH paper, filtering the chitosan residue with a 100 mesh filter cloth, then drying and calculating the yield of the deacetylation process again (Natalia et al., 2021).

2.3.6 Making Nanochitosan from Chitosan from Crab Shells

Preparation for making nanochitosan is carried out by sterilizing the tools and materials to be used using an autoclave. Then 1.5 grams of chitosan was dissolved using 15 ml of 1.5% acetic acid in a beaker while stirring until it formed a gel. After that, 50 ml of distilled water was added to the beaker gradually while stirring with a glass stirrer until homogeneous. Making nanochitosan using the ionic gelation method, making nanochitosan is carried out through three main stages, namely, depolymerization, emulsification and stabilization (Personal communication: Rozi, 2023).

Depolymerization is carried out using 2 units of the tokebi tool, where in this process, the solution that has been made in the preparation process is added to 150 ml of distilled water while stirring using the tokebi continuously without stopping, by changing the 2 units of the tokebi tool 8 times with a duration of 20 seconds . Emulsification was carried out using 20 µL of Tween 80 0.1% solution which was sprayed in stages 10 times every 5 seconds while the homogenization process with tokebi was running. Stabilization is carried out n using 100 ml of 0.1% NaTTP solution, add NaTTP gradually while the homogenization process with tokebi is running. Then the distilled water solution was added until it reached a total volume of 500 ml or ±135 ml while homogenizing with tokebi until a homogeneous nanochitosan solution was formed (clear in color) (Personal communication: Rozi, 2023).

2.4 Characterization

2.4.1 Fourier Transform Infrared Spectoscopy (FTIR) test and degree of deacetylation (DD)

The degree of deacetylation is calculated based on the formula according to research by Dompeipen (2017), as follows:

$$\%DD = 100 - \left(\frac{A1655}{A3450}\right) \times \frac{100}{1{,}33}$$

A1655 = Absorbance at wave number 1655 cm-1
A3450 = Absorbance at wave number 3450 cm-1
1.33 = Constant of the ratio of A1655 to A3450 for fully acetylated chitosan

2.4.2 Scanning Electron Microscopy

Examination of the characteristics and particle size of crab shell nanochitosan (Portunus pelagicus) using TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy) tests. 1 ml of nanochitosan solution was inserted into the medium that was fired with an infrared laser. The results obtained are the size values and index distribution of the particles in the solution.

2.5 Preparation Sample Solution For The Heavy Metal Iron

The process of making artificial waste uses the basic material FeSO4. 1.5 grams of H2O dissolved in 1000 mLlL of distilled water. The solution was stirred using a magnetic stirrer (room temperature) for 4 hours with 20 drops of HCl added. Next, artificial waste was tested using an atomic adsorption spectrophotometer (AAS) (Ali et al., 2018).

2.6 Adsorption Process

Adsorption was carried out in a previously prepared sample solution of the heavy metal iron (Fe). Nanochitosan with a dose according to the treatment. The solution was put into a 100 ml beaker, and 50 ml of heavy metal sample solution was added, then homogenization was carried out using nanochitosan which had been made with a magnetic stirrer at a speed of 180 rpm for 15 120 minutes with a magnetic stirrer. Treatment was carried out at room temperature. Then centrifugation was carried out at a speed of 5000 rpm for 2 hours to separate the residual concentration of the heavy metal Fe (Ali et al., 2018).

Effectiveness of crab shell nanochitosan adsorption

The percentage of effectiveness of adsorption efficiency is determined using the formula according to Ali et al. (2018):

$$R\% = 100 \times \frac{C_0 - C_e}{C_0}$$

R = Percentage of nanochitosan adsorption efficiency (%)
Co = Initial concentration (mg/L)
Ce = Final concentration (mg/L)

Data analysis

The data obtained is data on the reduction in levels of the heavy metal ion iron (Fe), then analyzed using statistical tests. The statistical test used in this research is Analysis of Variance (ANOVA) to determine whether there is a significant difference in the results of each treatment in real terms and, if in the ANOVA analysis there is a real difference then it will be continued with the Duncan 95% test to determine the difference between treatments. with other treatments.

2.7 Data Analysis

The data obtained is data on the reduction in levels of the heavy metal ion iron (Fe), then analyzed using statistical tests. The statistical test used in this research is Analysis of Variance (ANOVA) to determine whether there is a significant difference in the results of each treatment in real terms and, if in the ANOVA analysis there is a real difference then it will be continued with the Duncan 95% test to determine the difference between treatments. with other treatments.

3. RESULT AND DISSCUSION

3.1 Result

3.1.1 Chitosan

Making chitosan from crab shells (Portunus pelagicus) begins with grinding crab shells weighing ±2000 grams with a grinder at the Feed Laboratory, Faculty of Veterinary Medicine, Airlangga University. The grinding was carried out 3 times, where the first grinding was carried out with the aim of crushing the shells into flakes, the second grinding was carried out to grind the shell fragments, and the final grinding was carried out to produce fine crab shell powder. After grinding, the crab shell powder is sieved using a 100 mesh sieve to obtain a uniform size. The result of the grinding process is crab shell powder which has a fine texture like flour with a brownish white color, with a final weight after the grinding process of ± 680 grams.

Figure 1. Results of the crab shell grinding process. (A) Crab shells before grinding. (B) Crab shell powder that has been ground with a grinder machine and sieved with a 100 mesh sieve.

After the grinding process, crab shell powder is processed into crude chitin through a demineralization process with a ratio of 1:10 using 2M HCl and deproteinization using 3.5% NaOH at the Analytical Chemistry Laboratory of the Faculty of Science and Technology, Airlangga University. The final weight of crude chitin decreased from the initial weight of ±680 grams to ±130 grams or around 80.88% after the demineralization and deproteinization processes

The resulting crude chitin has a finer texture and brighter color than crab shell powder. The final process in processing crab shells into chitosan is the deacetylation process using 50% NaOH with a ratio of 1:10, the final weight resulting from the deacetylation process is ±6.7 grams. From the weight of the crude chitin produced, it was 130 grams and the final chitosan product weighed 6.7 grams, resulting in a yield value of 5.15%.

Table 1. Quality standards for crab shell chitosan

3.1.2 Nanochitosan

Figure 2. Results of nanochitosan which is dry or in powder form

The dried nanochitosan results are macroscopically white in color and shaped like flakes. Microscopic characterization of nanochitosan was carried out using a Scanning Electron Microscope (SEM), Particle Size Analyzer (PSA), and Fourier Transform Infrared (FTIR).

3.1.3 Scanning Electron Microscope (SEM)

*T*he scanning electron microscope (SEM) test was carried out at the Institute of Biological Sciences and Engineering, Airlangga University. SEM test results displayed in the form of 3-dimensional images were used to analyze the morphology of crab shell nanochitosan. The morphology of nanochitosan from crab shells based on the SEM test that has been carried out can be seen in Figure 14. It can be seen that the surface of the nanochitosan appears to have an irregular shape and some parts appear to have a round shape that is stacked up and some are flat, with an average size of 461 nm.

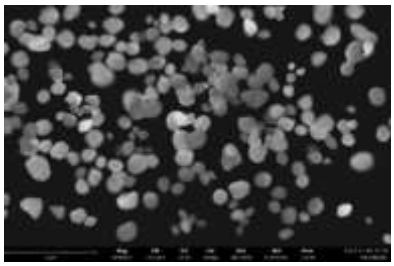

Figure 3. SEM test results of nanochitosan from crab shells with 40,000x magnification.

3.1.4 Fourier transform infrared (FTIR)

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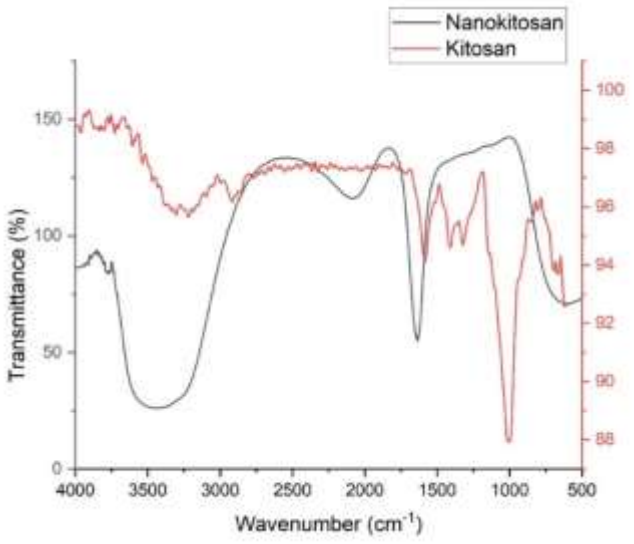

Figure 4. Wave spectra results of crab shell nanochitosan functional groups using FTIR

Based on the FTIR test, the functional group spectra in crab shell nanochitosan shows the stretching vibration of the O-H functional group at a wave number of 3446.79 cm-1. The wave number 2887.44 cm-1 shows the stretching vibration of the C-H functional group. At wave number 3446.79 cm-1 it shows bending vibrations from -NH2 stretching, and -NH2 bending at wave number 1600. At wave number 1656.85 cm-1 it shows stretching vibrations from the C=O functional group. At a wave number of 1300 cm-1, it shows stretching vibrations of the P=O stretching functional group.

Table 2. Functional groups of crab shell nanochitosan

No.	Functional GroupsCrab Shell Nanochitosan (cm-1)	Nadiyanto et al. 2019 (cm-1)	
1.	O-H stretch3446,793200 – 4000		
2.	-NH_2 stretch3446,793325 – 3500		
3.	C-H2887,442800 – 3000		
5.	-NH_2 bend	1600	1590 – 1650
6C=O1656,851649 – 1750			
7.	P=O (stretch)	1300	1250 – 1350

The FITR test can also be used to calculate the degree of deacetylation (%DD). Based on calculations, the degree of deacetylation of crab shell nanochitosan is 75.9%.

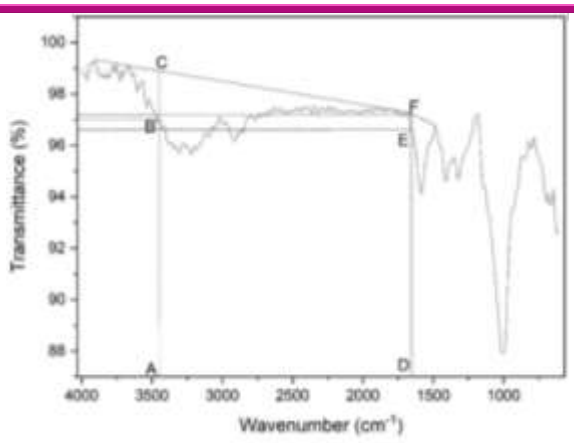

Figure 5. Projection of the origin of the calculation of the Degree of Deacetylation (%DD) of crab shell nanochitosan with FTIR spectrum values

3.1.5 Effectiveness of adsorption of crab shell nanochitosan (Portunus pelagicus) on the heavy metal ion iron (Fe)

The adsorption capacity of crab shell nanochitosan (Portunus pelagicus) on the heavy metal iron (Fe) can be measured using the atomic adsorption spectrophotometer (AAS) test. AAS is carried out with the aim of determining the adsorbance of an adsorbent on a compound containing metal. The basic principle in the AAS test is the interaction between the sample, namely crab shell nanochitosan, and electromagnetic radiation. AAS is the most efficient and economical method.

Table 3. Calculation results of the effectiveness of absorption of the heavy metal ion iron (Fe) using naokitosan from crab shells (Portunus pelagicus)

No.	Treatment	C0 (mg/L)	Ce (mg/L)	Effectiveness (%)
1.	Negative control	50	49,64	0,72±0,47
2.	Positive control	50	17,81	64,38±0,47
3,	P1	50	15,79	68,41±0,46
4.	P2	50	14,37	71,27±0,76
5.	P3	50	12,71	74,59±0,54
6.	P4	50	10,85	78,30±0,11
7.	P5	50	8,63	82,75±0,20

Based on the Shapiro-Wilk normality statistical test, it can be seen that the data is normally distributed with a p value > 0.05, with the treatment group values (P0, P1, P2, P3, P4, P5, and P6) having values respectively 0.97; 0.71; 0.19; 0.32; 0.22; 0.41; 0.54. The homogeneity test results show a p value of 0.064 (p>0.05), which means the data is homogeneous. Then, based on the Analysis of Variance (ANOVA) carried out on the adsorption capacity of crab shell nanochitosan as a bioadsorbent, it had a significant effect on the absorption of the

heavy metal ion iron (Fe) in water. Based on the Duncan test results, there were 7 treatment groups with the percentage of adsorption effectiveness indicated by 7 different letters, namely (a, b, c, d, e, f, and g). This shows that there are real differences in each treatment.

Based on the results of the atomic adsorption spectrophotometer (AAS) test, the concentration of the heavy metal iron Fe (II) was reduced by 50 mg/L by adding bioadsorbent in the form of chitosan of 100 mg/L as a positive control and nanochitosan according to the treatment (25 mg/L; 50 mg/ L, 100 mg/L, 200 mg/L, and 400 mg/L). In the treatment without adding chitosan and nanochitosan to the solution, there was a decrease of up to 49.64 mg/L or an effectiveness value of 0.72 ± 0.47%. The addition of 100 mg/L of chitosan resulted in a reduction of up to 17.81 mg/L or an effectiveness value of 64.38 ± 0.47%.

3.2 Discussion

The quality of chitosan in this research can be seen in Table 1 which shows that the chitosan produced meets SNI No. 7949 of 2013. The chitosan produced has a white color, with a water content of 8.66%, an ash content of 0.95%, and a degree of deacetylation of 95 ,44%,. The degree of deacetylation of the crab shell chitosan produced in this study was much higher, but had a lower water content than in the study by Fatnah et al. (2019), which produces chitosan with a deacetylation degree of 79.68% with a water content of 5.2%. Based on research conducted by Hao et al. (2021), the ash content of crab shell chitosan is higher with a value of 0.6%. Meanwhile, according to research conducted by Natalia et al. (2021), the water content and ash produced are higher with values of 11.25-12.93%; and 1.62-1.75%; However, the degree of deacetylation produced was lower with a value of 57.64%.

The difference in quality scores resulting from this research and research by Fatnah et al. (2019); Hao et al. (2021); and Natalia et al. (2021) can be caused by the concentration of chemicals used and the methods used. The difference in the degree of deacetylation produced is influenced by the concentration of chemicals, contact time, pH and temperature in the manufacturing process. High concentrations of NaOH in the deacetylation process can result in the amine functional group substituting for the acetyl group in chitin, so that the degree of

3.2.1 Nanochitosan

In this research, the raw material in the form of crab shell chitosan was processed into nanochitosan using the ionic glassic method which involved the use of a 12,000 rpm homogenizer. Making nanochitosan is divided into three main stages, namely depolymerization, emulsification and stabilization. Depolymerization has the function of cutting the chitosan polymer chain which initially numbered 3000 monomers into 10 monomers. Emulsification uses chemicals in the form of Tween 80 with a concentration of 0.1% which functions to homogenize and emulsify chitosan. In this process the chitosan which was initially elongated in shape will change to a spherical shape which is nano-sized or called micellar, but the nano-spheres that are formed are It is not yet stable, breaks easily, and can form polymer chains again, so a final process is needed, namely stabilization.

The stabilization process in this research uses sodium tripolyphosphate (NaTTP). NaTTP functions as a crosslinker that binds positively ionized chitosan (-NH2+) with polyanions from tripolyphosphate (TTP), so that the matrix that has been ah formed to be stronger and more stable. According to Koukaras et al. (2012) in a scientific article entitled "Insight on the Formation of Chitosan Nanoparticles through Ionotropic Gelation with Tripolyphosphate", the ionic glassic method is the easiest and most efficient method for making nanochitosan, in the ionic glassic method, the polymer chains of chitosan can be converted into monomers . In acidic solutions, chitosan oligomers can form nanoparticle sizes through ionic cross-linking with multivalent anions, through these bonds micelles will be formed with more stable conditions.

3.2.2 Scanning Electron Microscope (SEM)

Based on the scanning electron microscope (SEM) test in this study, the surface morphology of crab shell nanochitosan, where the surface of the nanochitosan appears to have an irregular shape and some parts appear to have a rounded shape that is stacked and some are flat. The SEM test results carried out in this research are not much different from research conducted by Ali et al. (2018), where the nanochitosan from crab shells in their research which was tested using SEM has the characteristics of an amorphous (shapeless) polymer and is round in shape and has a porous layer with high porosity.

Based on the scanning electron microscope (SEM) test, it shows that the distribution of nanochitosan size values from crab shells in this study has an average of 461 ± 0.957 nm. The results of the size of crab nanochitosan produced in this study were larger than the results of research conducted by Ali et al. (2018), where the size of the crab naokitosan produced is 50-100 nm. According to Divya and Jisha. (2018) Nanoparticles in general are solid particles that have unique properties with equivalent mass because the decrease in size occurs at the atomic level. Nano-sized particles have constant properties, however, as the particle size decreases, the percentage of surface atoms will decrease. According to Abdelnaby et al. (2023), chitosan nanoparticles are a solid colloid that has a size of 1-1000 nm with a large surface area and is easily decomposed scientifically so that it has high reactivity and adsorption potential in extracting metal ions from water.

3.2.3 Fourier transform infrared (FTIR)

According to Nandiyanto et al. (2019), the FTIR test is a tool used to analyze and characterize samples in the form of liquid, solution, powder, paste, fiber, gas and film. This tool is used to analyze the material contained in a sample, where with this tool a sample can be characterized with high accuracy in a fairly fast time. In the procedure for using an FTIR tool, the sample will be exposed to infrared (IR) radiation, which

creates vibrations in the atoms and molecules contained in the sample and causes energy transmission to determine the vibrations of specific molecules contained in a sample.

Chitosan has a main functional group consisting of the hydroxyl functional group (O-H); amine (N-H); and carbonyl (C-O). In the results of the research carried out, the results of the interpretation of functional groups based on wave values are not much different from research conducted by Fatnah et al. (2019), namely that there is an absorption wave number of 3361.86 cm-1 which shows the vibration of the O-H group; absorption at 2876.71 cm-1 indicates stretching vibration of the C-H group; The C=O amide group appears with an absorption wave number of 892.57 cm-1 indicating the presence of the NH2 functional group at an absorption wave number of 1148.86 and vibration of C-

O-C is indicated by the absorption wave value of 1031.27 cm-1. In the nanochitosan functional group from crab shells, there is a removal of the acetyl functional group due to the deacetylation process, where at this stage the acetyl group will react with the hydroxyl group and produce an amine group. This is in accordance with the opinion of Fatahu et al. (2015), which contains and has functional group values that are not much different from the research carried out.

The number of acetyl groups that are deacetylated becomes The amine group in chitosan is shown to have weakened and lost hydrogen bonds. The number of acetyl groups that are deacetylated to become amine groups in chitosan is indicated by the lower intensity of the absorption peak of the C=O group (NHCOCH3, amide I). The lower the intensity of the absorption peak of the C=O group, the higher the degree of chitosan deacetylation (Purnawan et al. 2009). In addition, the more acetyl groups released cause a shift towards a smaller wave number in the absorption of the C=O group (NHCOCH3, amide I) towards the absorption (-NH2, amine). The C=O bond from the acetyl group has a greater strength than the N-H bond strength from the amine group (Purnawan et al. 2009), the strength of the bond is directly proportional to the vibrational energy and wave number. The functional groups contained in nanochitosan play a role in the adsorption process, where heavy metal ions attach to the surface of nanochitosan, and cause chelation and complexation. The layer formed from the complexation process by hydroxyl groups (O-H) on heavy metal ions is then separated by filtering the adsorption water with Whatman No. 42 filter paper, resulting in a reduction in heavy metals in the water. Chelation is the main process for removal by forming coordinate covalent bonds with metal ions, while some hydroxyl groups can also take part in coordination with the release of protons (Ali et al., 2018). Surface complexation occurs between metal ions and functional groups containing oxygen atoms on nanochitosan, by sharing lone electron pairs on oxygen atoms (Alyasi et al., 2021).

3.2.4 Effectiveness of adsorption of crab shell nanochitosan (Portunus pelagicus) on the heavy metal ion iron (Fe)

Based on the results of the adsorption effectiveness test for crab shell nanochitosan (Portunus pelagicus), the results obtained can be seen in Table 6. Where it can be seen that the optimum dose of crab shell nanochitosan as a bioadsorbent is at a dose of 400 mg/L with an effectiveness value of 82.75%. Based on the results obtained, when compared with research conducted by Ali et al. (2018), showed that the adsorption results of nanochitosan from crab shells turned out to have a lower value than nanochitosan from shrimp shells in adsorbing the heavy metal ion iron (Fe). This can be influenced by several main factors such as temperature, pH, contact time, and the type of adsorbent used. Shrimp shells have a greater amount of chitin than crab shells, this also causes the adsorption of nanochitosan with crab shells to be less than crab shells. This is in line with research conducted by Elabbas et al. (2016), namely the amount adsorbed from the solution depends on a number of factors such as the nature of the adsorbent and adsorbate, the interfacial tension between the solution and the adsorbent, temperature, concentration, porosity of the adsorbent, pH of the solution, ionic competition, the presence of foreign materials, time and treatment. carried out in adsorption.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusion

Based on the research conducted, it can be concluded that, the effectiveness value of crab shell nanochitosan as a bioadsorbent is 68.41 ± 0.46% to 82.75 ± 0.2%. The optimum dose of crab shell nanochitosan as a bioadsorbent is at a dose of 400 mg/L

4.2 Suggestion

Further tests are needed on other parameters such as temperature, pH, contact time, which can affect the quality of nanochitosan as a bioadsorbent to reduce levels of the heavy metal ion iron (Fe),

5. REFERENCES

[1] Abbas, E. M., Abdelsalam, K. M., Mohammed-Geba, K., Ahmed, H. O., and Kato, M. 2016. Genetic and morphological identification of some crabs from the Gulf of Suez, Northern Red Sea, Egypt. The Egyptian Journal of Aquatic Research, 42(3): 319-329

[2] Abdelnaby, A., Abdelaleem, N. M., Elshewy, E., Mansour, A. H., and Ibrahim, S. S. (2023). Application of bentonite clay, date pit, and chitosan nanoparticles as promising adsorbents to sequester toxic lead and cadmium from milk. Biological Trace Element Research, 201(5): 2650-2664.

[3] Ali, A. S., Ameen, U. S., Farid, M., Bharwana, A. A., Hannan, F., and Ahmad, R. 2014. Effect of different heavy metal pollution on fish. Res. J. Chem. Environ. Sci, 2(1): 74-79.

[4] Ali, M. E. A., Aboelfadl, M. M. S., Selim, A. M., Khalil, H. F., and Elkady, G. M. 2018. Chitosan nanoparticles

extracted from shrimp shells, application for removal of Fe (II) and Mn (II) from aqueous phases. Separation Science and Technology, 53(18): 2870-2881.

[5] Alyasi, H., Mackey, H., and McKay, G. 2021. Novel model analysis for multimechanistic adsorption processes: case study: cadmium on nanochitosan. Separation and Purification Technology, 1–29.

[6] Badan Standardisasi Nasional. 2013. Kitosan – Syarat Mutu dan Pengolahan. SNI No. 7949.2013. Jakarta : Dewan Standardisasi Nasional.

[7] Kementrian Kelautan dan Perikanan. 2020. BBPBAP Jepara Jadikan Lamongan Kampung Rajungan. https://kkp.go.id/djpb/bbpbapjepara/artikel/18030-bbpbap-jepara-jadikan-lamongan-kampung-rajungan. Diakses pada 1 Mei 2023.

[8] Benettayeb, A., Seihoub, F. Z., Pal, P., Ghosh, S., Usman, M., Chia, C. H., and Sillanpää, M. 2023. Chitosan Nanoparticles as Potential Nano-Sorbent for Removal of Toxic Environmental Pollutants. Nanomaterials, 13(3): 447-45

[9] Borah, P., Kumar, M., and Devi, P. 2020. Types of inorganic pollutants: metals/metalloids, acids, and organic forms. In Inorganic pollutants in water (pp. 17-31). Elsevier.

[10] Dar, A. H., Rashid, N., Majid, I., Hussain, S., and Dar, M. A. 2020. Nanotechnology interventions in aquaculture and seafood preservation. Critical Reviews in Food Science and Nutrition, 60(11): 1912-1921.

[11] Divya, K., and Jisha, M. S. 2018. Chitosan nanoparticles preparation and applications. Environmental chemistry letters, 16: 101-112.

[12] Djaenudin, D., Budianto, E., Saepudin, E., dan Nasir, M. 2019. Ekstraksi kitosan dari cangkang rajungan pada lama dan pengulangan perendaman yang berbeda. Jurnal Teknologi Perikanan dan Kelautan, 10(1): 49-59.

[13] Emenike, E. C., Iwuozor, K. O., and Anidiobi, S. U. 2021. Heavy metal pollution in aquaculture: sources, impacts and mitigation techniques. Biological Trace Element Research, 20: 4476 -4492

[14] Farihin, F. M., Wardhana, I. W., dan Sumiyati, S. 2015. Studi Penurunan COD, TSS, dan Turbidity Dengan Menggunakan Kitosan dari Limbah Cangkang Kerang Hijau (Perna viridis) Sebagai Biokoagulan Dalam Pengolahan Limbah Cair PT. Sido Muncul Tbk, Semarang. Doctoral dissertation. Universitas Diponegoro.

[15] Fatahu, F., Natsir, H., and Taba, P. 2015. Synthesis and Characterization of Chitosan Nanoparticles from the shells of crabs (Portunus pelagicus) and Application as Antimicrobial. Jurnal Akta Kimia Indonesia (Indonesia Chimica Acta), 8(2): 17-28.

[16] Fatnah, N., Azizah, D., and Cahyani, M. D. 2020. Synthesis of chitosan from crab's shell waste (Portunus pelagicus) in mertasinga-cirebon. In International Conference on Progressive Education, 370-375.

[17] Hao, G., Hu, Y., Shi, L., Chen, J., Cui, A., Weng, W., and Osako, K. 2021. Physicochemical characteristics of chitosan from swimming crab (Portunus trituberculatus) shells prepared by subcritical water pretreatment. Scientific Reports, 11(1): 1646.

[18] Iwuozor, K. O., Oyekunle, I. P., Oladunjoye, I. O., Ibitogbe, E. M., and Olorunfemi, T. S. 2022. A review on the mitigation of heavy metals from aqueous solution using sugarcane bagasse. Sugar Tech, 24(4): 1167-1185.

[19] Kementrian Lingkungan Hidup. 2014. Peraturan Menteri Lingkungan Hidup Republik Indonesia Nomor 5 Tahun 2014 Tentang Baku Mutu Air Limbah. Jakarta: KLH.

[20] Kementerian Lingkungan Hidup dan Kehutanan. 2021. Buku Statustik Kualitas Air, Udara, dan Tutupan Lahan Tahun 2020. Jakarta: Direktorat Jenderal Pengendalian Pencemaran dan Kerusakan Lingkungan.

[21] Koukaras, E. N., Papadimitriou, S. A., Bikiaris, D. N., and Froudakis, G. E. 2012. Insight on the formation of chitosan nanoparticles through ionotropic gelation with tripolyphosphate. Molecular pharmaceutics, 9(10): 2856-2862.

[22] Madhavi, T. P., and Rajkumar, R. 2013. Utilisation of Natural Coagulant for Reduction of Turbidity from Wastewater. International Journal of Chemtech Reseacrh, 5(3): 1119-1123.

[23] Nandiyanto, A. B. D., Oktiani, R., and Ragadhita, R. 2019. How to read and interpret FTIR spectroscope of organic material. Indonesian Journal of Science and Technology, 4(1): 97-118.

[24] Natalia, D. A., Dharmayanti, N., dan Dewi, F. R. 2021. Produksi kitosan dari cangkang rajungan (Portunus sp.) pada suhu ruang. Jurnal Pengolahan Hasil Perikanan Indonesia, 24(3): 301-309.

[25] Nugroho, R. P., Daud, S., dan Asmura, J. 2018. Penyisihan Kadar Fosfat Pada Limbah Cair Laundry Menggunakan Biokoagulan Cangkang Keong Mas (Pomacea Canaliculata). Jurnal Online Mahasiswa (JOM) Bidang Teknik dan Sains, 5: 1-5.

[26] Nugroho, I. L., Masithah, E. D., & Pursetyo, K. T. 2020, February. The effect of hydrochloric acid concentration and temperature demineralization on characteristics of chitin from penshell (Atrina pectinata). In IOP Conference Series: Earth and Environmental Science (Vol. 441, No. 1, p. 012152). IOP Publishing.

[27] Peraturan Pemerintah Nomor 82 Tahun 2001 Tentang Pengelolaan Kualitas Air dan Pengendalian Pencemaran Air.

[28] Purnawan, C., Aprilita, N. H., Kartini, I., & Sugiharto, E. (2009). Kajian Parameter Deasetilasi Kitin dari Cangkang Udang Berdasarkan Karakter Spektra Infra Merah (IR). In Prosiding Seminar Nasional Kimia Dan Pendidikan Kimia (pp. 499-513).

[29] Sari, A. M., Hendrawati, T. Y., Ananda, K. R., dan Erdawati, E. 2020. Pengaruh Variasi Massa Kitosan Terhadap Yield Dalam Pembuatan Nanoemulsi Kitosan Dengan Metode Gelasi Ionik Dan Freezing. Jurnal Teknologi, 12(2): 107-122.

[30] Sasidharan, A. P., Meera, V., and Raphael, V. P. 2021. Investigations on characteristics of polyurethane foam impregnated with nanochitosan and nanosilver/silver oxide and its effectiveness in phosphate removal. Environmental Science and Pollution Research, 28: 12980-12992.

[31] Sisyanreswari, H., Oktiawan, W., dan Rezagama, A. 2014. Penurunan TSS, COD, dan fosfat pada limbah laundry menggunakan koagulan tawas dan media zeolite. Doctoral Dissertation. Universitas Diponegoro.

[32] Suriawan, A., Efendi, S., Asmoro, S., dan Wiyana, J. 2019. Sistem budidaya udang vaname Litopenaeus vannamei pada tambak hdpe dengan sumber air bawah tanah salinitas tinggi di kabupaten Pasuruan. Jurnal Perekayasaan Budidaya Air Payau dan Laut, 14: 6-14.

[33] Sutrisno, S., Koesoemadinata, S., dan Taufik, I. 2016. Tingkat pencemaran logam berat pada ekosistem waduk di Jawa Barat (Saguling, Cirata, dan Jatiluhur). Jurnal Riset Akuakultur, 2(1): 103-115.