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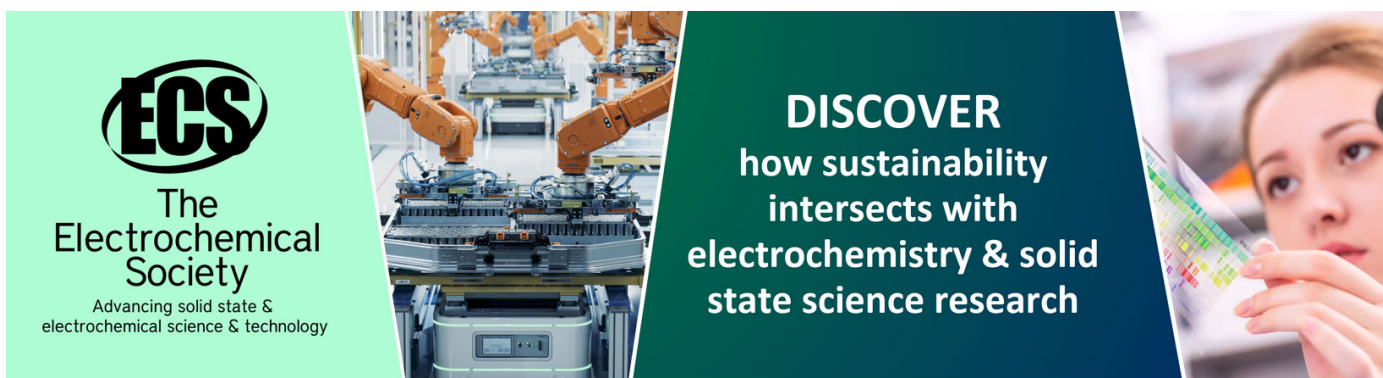
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Identification of chitosan beads from coconut crab patani variety using Fourier Transform Infrared Spectroscopy (FTIR)

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Abstract. This study aims to synthesize and characterize chitosan beads using the Fourier Transform Infra Red (FTIR) spectrophotometer. The test was carried out by making chitosan beads by mixing chitosan and 0.1 M acetic acid and dropping it into 0.1 M NaOH solution to form gel beads. Based on the results of the study obtained the value of the degree of deacetylation of chitosan by 76.85% and chitosan beads by 89.32%. While the characterization of chitosan beads based on FTIR spectrophotometer showed a difference in the peak absorption of NH_3 at wave number 1450.47 cm^{-1} with a slightly wider band on the chitosan beads while the sharp NH_2 absorption band appeared in the region of 1435.04 cm^{-1} in chitosan. And there is an absorption peak in the region of 570.93 cm^{-1} which is the KBR absorption peak used as pellets in chitosan samples.

1. Introduction

Patani is a coastal village in North Maluku, Indonesia, located on the eastern peninsula of Halmahera. It is located within the Central Halmahera Regency. Geographically, Patani is at the far end and dealing directly with Raja Ampat Regency, West Papua. Patani has a good fishery climate where a large number of coconut crabs are found on this island, so that the Central Halmahera Regency Government is used as a breeding place for coconut crabs. Coconut crabs that are bred into fishery commodities are very promising. The potential of coconut crabs on Yoi Island is estimated at 3,513,600-5,270,400 tails (per station) or 4,522,133 tails (total stations). To avoid mortality which is quite high in nature, the crab is quite suitable for cultivation include magrove [1]. Coconut crabs are sold to restaurant entrepreneurs and some are even exported to neighboring countries. The meat is consumed, the skin is left to be worthless waste [2].

One source of chitosan comes from waste such as; shrimp shells, crab shells and so on. In Indonesia as an exporting country of crab resources, based on the data from Directorate General of Strengthening Competitiveness of Marine Products and Fisheries in 2019, the total volume of origin of Indonesian raw material exports of crab and crab in frozen, fresh and processed forms is 27,367,452 with an export value of (US\$) 411,361,616 with America, Japan and China as the main export destination countries. However, not a few problems that arise due to these crabs. In 2000 the Ministry of Maritime Affairs and Fisheries released the export of canned crabs by 4000 tons, and produced skin as waste by 1000 tons. Thus the need for crab management produces waste in the form of shells that cannot disturb the environment. Chitosan is a natural polymer compound from the deacetylation process to remove the acetyl group in chitin.

According to [3][4] the results of chitosan research from catfish and mackerel obtained a degree of deacetylation of 61.08% while chitosan in tiger shrimp shells [5][6] obtained degrees of deacetylation of 81.11% a degree of deacetylation was obtained at 77.84%. Chitosan is a cationic polymer that is non-toxic and has biodegrading and biocompatible properties that chitosan possesses. Chitosan can be used



in various industrial fields such as pharmaceutical, food, textile, biochemistry, cosmetics, nutrition, paper and health [7]. Modification of chitosan has NH_2 group and can provide a pair of free and reactive electrons to other compounds because chitosan is easy to be modified into beads so that the structure of chitosan is more ordered [8][9][10]. Chitosan can be made into chitosan beads, so it does not dissolve easily in acids and will be used more widely. Because dilute weak acids in the chitosan beads matrix will cause the NH_2 chitosan beads group to have a higher affinity than chitosan. Chitosan beads are modifications of the chitosan matrix so that they can expand gradually and will expand in acidic media. One of the beads is obtained from a hydrophobic surface to avoid the dispersion of chitosan in the medium.

2. Research Methods

Research scope, Observational and experimental research which included the production of chitosan compounds (through the stages of chitin) from coconut crab shells and characterization of chitosan beads. The study was conducted at the Environmental Laboratory, Faculty of Teacher Training and Education, Khairun University. **Material and Tools**, For materials, among others; coconut crabs shells, CH_3COOH , NaOH , aquades, filter paper, and pH indicator paper, NaOCl , AgNO_3 and iodine salt. The tools used include magnetic stirrers, pH meters, analytical procedures, a set of glassware, dropper pipettes, funnels, stirring rods, shakers, ovens and Infrared Spectrophotometers (FTIR). **Chitosan production stages from coconut crabs skins**. Wash crab skin with clean water, then stir in the sun. After that, the crab shell waste can be mashed to get a size of 50 mesh. **Deproteination**, Crab skin powder is mixed with a solution of NaOH at a ratio of 1:10 (g/mL), heated at 65°C . After chilling filtered and neutralized with distilled water to neutral pH. The solids are dried in an oven at 80°C for about 5 hours. After that it is weighed to a constant weight [11]. **Demineralization** Deproteination powder was mixed with 1.5 M HCl solution at a ratio of 15: 1 (g/mL) [12] [13]. Then the mixture is stirred for about 1.5 hours and rinsed with distilled water to neutral pH. Identification of Cl^- solution was tested using AgNO_3 solution to see the formation of white precipitate, if the white precipitate was absent then the Cl^- ion was lost. The solid is stirred in an oven at 65°C for about 5 hours. After that it is weighed to a constant weight. **Depigmentation**, Demineralization powder was mixed with 3% NaOCl solution at a ratio of 1:10 (g / mL) [14]. The mixture is stirred for 1.5 hours without heating, the mixture is filtered and rinsed with distilled water to neutral pH. The solids are dried in an oven at 65°C for about 5 hours. After that it is weighed to a constant weight to obtain a sample in the form of napkin. The powder obtained is Chitin powder. Then the chitin obtained was characterized by the Van Wesslink color reaction, reacting the dry powder obtained above with iodine salt (KI-12) 1.5%, if positive containing chitin would give a brown color. The next step was tested using FTIR.

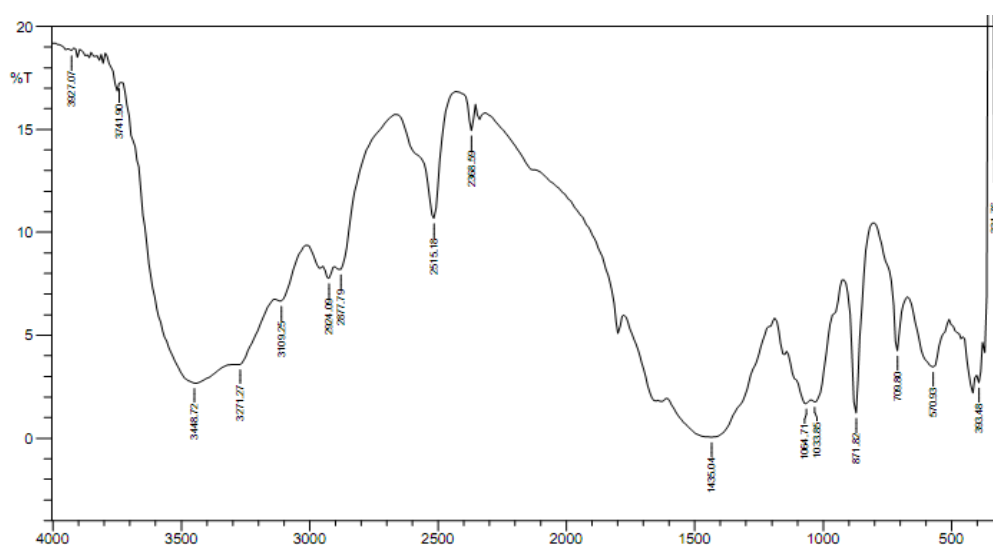


Figure 1. FTIR spectra of chitin coconut crab from pigmentation results.

Chitosan was made through the process of deacetylation of chitin by following the Knorr method, namely by adding 60% NaOH at a ratio of 10: 1 (g/mL) and put into the extractor at 80°C for 1 hour. After chilling is filtered and the solids obtained are neutralized with distilled water. The solid is then dried in an extractor without solution at 80°C for 5 hours and chitosan is ready to be analyzed. Furthermore, the chitosan obtained was analyzed using the FTIR method to determine the degree of deacetylation (DD) [15]. To determine DD used the line method by Moore and Robert. The sample is made of pellets in KBr powder and then the spectrum is determined [16][17][18]. The formula of Degree of Deacetylation DD as follow:

$$DD = \left[1 - \left[\frac{A_{1588}}{A_{3410}} \times \frac{1}{1,33} \right] \right] \times 100\%$$

Annotation:

A = $\log (P_o/P)$ = absorbance

A_{1588} = Absorbance at wavelength of 1588 cm^{-1} for absorption of amide/acetamide groups (CH_3CONH^-)

A_{3410} = Absorbance at wavelength 3410 cm^{-1} for absorption of hydroxyl groups (OH^-)

3.Results and Discussion

3.1. Identification coconut crubs from Patani Central Halmahera



Figure 2. Coconut crubs from Patani Central Halmahera

Coconut Crubs or known as *Birgus Latro* [19] [20] [21]. Generally its sizes up to 40 cm and streshes up to 220 cm. Moreover it divided into the head and chest with 10 legs and the abdomen. The colour is generally blue-purple-brown, also having hands with shreds of powder used to scratch, peel coconut, lifting objects even up to 30 kg. In addition, Coconut Crubs also have several pairs of legs which are used to help them hold things and climbs trees to a height of 10 m, so that they can climb coconut trees to take fruit using shreds and take coconut meat to eat.

This research has been carried out making chitosan from coconut crab shells and characterization of chitosan beads. Some of the stages that will be discussed in this study are; First, explain the principle of the procedure for making chitosan beads until the target product is formed. Second, explaining qualitatively the quality of chitosan beads formed through a FTIR characterization method so that it can be ensured that the starting material (chitosan powder) has been converted at a certain level of DD percentage into a target product (chitosan beads).

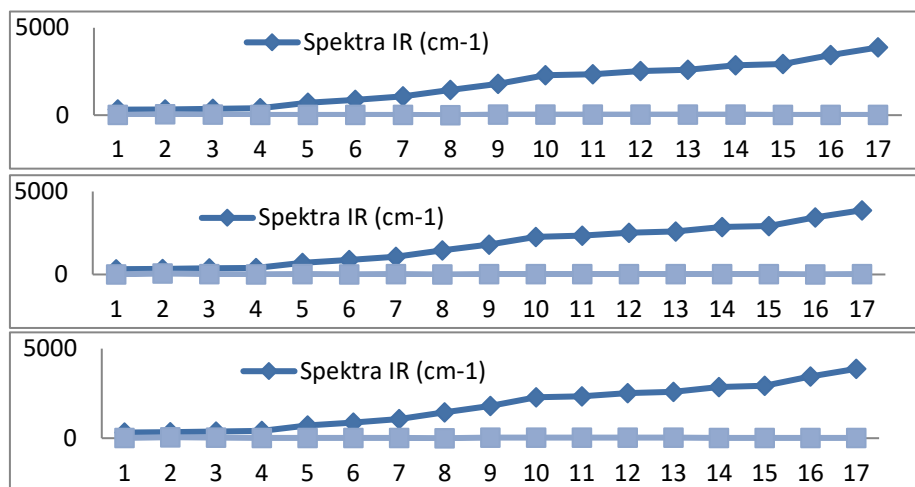


Figure 3. Standard data on chitosan beads

3.2 Chitosan powder in acetic acid solution

Making chitosan beads by dissolving chitosan into acetic acid (CH_3COOH) to remove inorganic salts in chitosan. After that it can form O_2 gas in the form of air bubbles when acetic acid is added to the sample, and initially chitosan and acetic acid (CH_3COOH) are mixed together using a shaker at a stirring speed of 150 rpm, a time of 30 minutes. So that the chitosan solution can be mixed perfectly. acetic acid (CH_3COOH) as a solvent and has an H^+ group and can break the long chain bonds of chitosan polymers into smaller polymers.

3.3 Formation of beads with NaOH solution

NaOH solution is made by dissolving NaOH in water. In the solution ionic compounds will become ions so that NaOH will also become sodium ions (Na^+) and hydroxide ions (OH^-). Because chitosan has the ability to ensnare other compounds. At this stage the viscous chitosan solution in acetic acid that has been obtained, is taken with a dropper dropper and dipped dropwise into a glass beaker containing NaOH solution at 50°C and kept temperature for approximately 1 hour. So that the solution formed will coagulate and form beads [22]. Preparations were made with several variations on the component beads to find chitosan beads in terms of shape and size. After 1 hour the beads formed are separated from the solution and dried using filter paper. After washing the beads, it is heated in the oven for 30 minutes to a constant. After that, the beads that are formed are prepared to be carralized with FTIR.

3.4 Characterization of chitosan and chitosan beads using FTIR

Several research results have been published [23] [24] [25] shows that chitosan and chitosan beads do not show significant differences. This result is indicated through FTIR analysis that the change in the structure of chitosan to chitosan beads hardly changes the position of the functional group at all, but only a shift of several wavelength values (within a certain range) and changes in intensity. Regarding the arguments above, the author will present data on the results of the characterization of FTIR chitosan and chitosan beads seen in the following spectra:

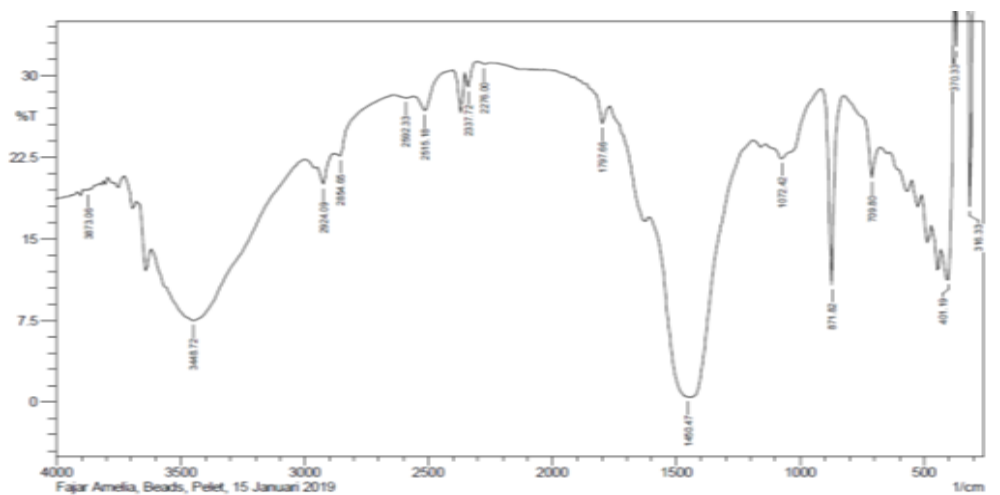


Figure 4. FTIR spectra of chitosan coconut crab

In figure 4 (chitosan) and 5 (chitosan beads) there are differences. Based on FTIR data, in general the absorption band can be divided into three regions. First, the absorption band in the region (3000-3700) cm^{-1} is a stretching band for the -OH group and the -NH group. Second, the absorption band in the region (1400-4000) cm^{-1} is a special absorption band to identify various functional groups; and third, the area to the right of 1400 cm^{-1} is the fingerprint region. In this fingerprint area, absorption bands often experience a high level of complexity due to the mode of vibration stretching and bending/bending vibrations that occur overlapping or overlapping [26][27].

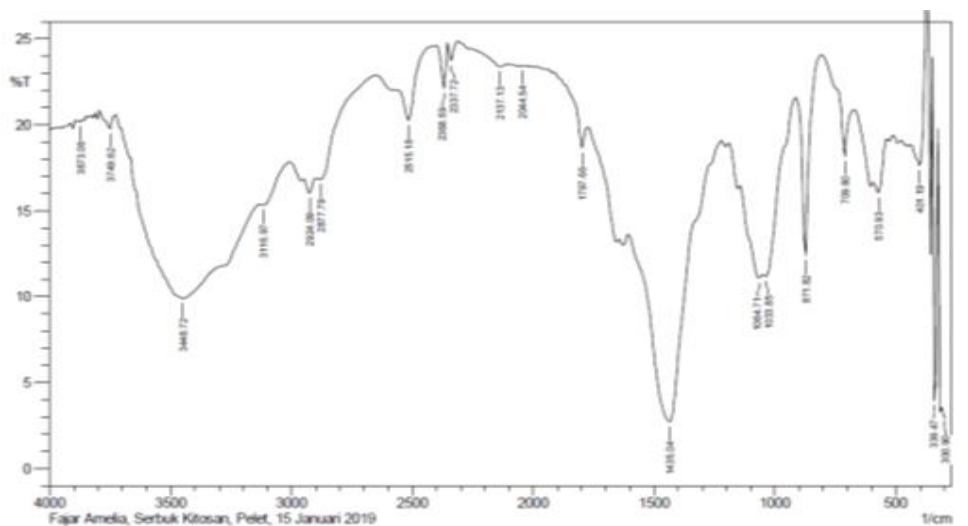


Figure 5. FTIR spectra of coconut crab chitosan beads

FTIR data also shows that the absorption band width in the area of 3448.72 cm^{-1} is clearly the OH absorption band, but two weak absorption bands between 3748.82-3873.06 cm^{-1} in chitosan can be believed to be a possible absorption band -NH originating from the amide group, it's just that it has shifted from 3700 cm^{-1} because it might be influenced by solvent factors [28]. After adding 0.1 M acetic acid in 0.1 M NaOH (as a process of forming beads), there was a weak absorption in the area of 3748.82 cm^{-1} , followed by an area of 3116.97 cm^{-1} , then in the area of 2137, 13 cm^{-1} and 2044.54 cm^{-1} . The loss

of absorption peaks is marked by the loss of a small portion of NH- group absorption (from amide, 3748.82 cm^{-1}), stretching vibration -CH (3116.97 cm^{-1}), and loss of a small amount of stretching vibration of the -N $\equiv$ group C- ($2137.13\text{--}2044.54\text{ cm}^{-1}$) [29] contained in the chitosan content [30].

On the other hand, the appearance of weak absorption bands in the area of 2592.33 cm^{-1} on chitosan beads can be indicated as the emergence of stretching vibrations - N-CH₂ [31]. In addition, there has been a change in the strong absorption band in chitosan (two peaks) in the area of 1064.71 cm^{-1} and 1033.85 cm^{-1} in chitosan to a weak absorption peak in chitosan beads in the area of 1072.42 cm^{-1} . This could indicate that some amide groups were converted to amine groups (arrow 1) and some protons (from acetic acid) had been added as an advanced mechanism to convert to -NH₂ groups.

The loss of stretching vibration -CH in the region of 3116.97 cm^{-1} may be influenced by bond polarization due to the degree of polarity of acetic acid so that it shifts to a lower wave number and appears in the region of 1450.47 cm^{-1} with the band slightly wider than the chitosan band.

On the other hand, sharp absorption peaks in the area of 1064.71 cm^{-1} and 1033.85 cm^{-1} in chitosan show typical absorption of the -CO group on CH₂-OH and overlap with the -CO group on the ether -COC- bond (pyranose ring). This absorption becomes weak and only one peak in the area of 1072.42 cm^{-1} (arrow 6) on chitosan beads due to the influence of the formation of hydrogen bonds from NH₃. Typical absorption bands of the sharp -NH₂ group appear in the region of 871.82 cm^{-1} , both in chitosan and chitosan beads. The addition of acetic acid in NaOH causes the loss of absorption band in the region of 570.93 cm^{-1} in chitosan (arrow 7) and the absorption peak in the region of 401.19 cm^{-1} in chitosan beads is slightly sharper than the absorption peak in chitosan. It can be believed that the absorption peak in the region of 570.93 cm^{-1} is the peak of KBr absorption which is used as a pellet in chitosan samples [32] and disappears due to the possible influence of hydrogen bonds formed (in NH₃⁺) so as to increase the intensity at area of 401.19 cm^{-1} in chitosan beads [31].

4. Conclusion

1. The DD values of chitosan from coconut crab shell of patani variety is 76.85% and chitosan beads are 89.32%.
2. The FTIR values of characterization chitosan beads c shows the difference in the NH₃ absorption peak in the 1450.47 cm^{-1} wave with a slightly wider band on the chitosan beads. Meanwhile a sharp NH₂ absorption band in the 1435.04 cm^{-1} area of chitosan. The absorption peak in the area of 570.93 cm^{-1} is the peak absorption of KBR used as a pellet in the chitosan.

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References;

- [1] M. Z. Rahman and D. Pansyah, "Pemberdayaan Ekonomi Masyarakat Pesisir Melalui Pemanfaatan Hutan Mangrove Untuk Budidaya Kepiting Bakau Desa Eat Mayang Sekotong Timur Lombok Barat," *J. Kaji. Penelit. Pengemb. Pendidik.*, 2019.
- [2] D. B. Hungria, C. P. dos Santos Tavares, L. Â. Pereira, U. de Assis Teixeira da Silva, and A. Ostrensky, "Global status of production and commercialization of soft-shell crabs," *Aquaculture International*. 2017, doi: 10.1007/s10499-017-0183-5.
- [3] Rika Silvia, Sari Wahyu Waryani, and Farida Hanum, "Pemanfaatan Kitosan Dari Cangkang Rajungan (*Portonius sanguinolentus* L.) Sebagai Pengawet Ikan Kembung (*Rastrelliger* sp) dan

- Ikan Lele (*Clarias Batrachus*),” *J. Tek. Kim. USU*, 2015, doi: 10.32734/jtk.v3i4.1651.
- [4] Sari Wahyu Waryani, Rika Silvia, and Farida Hanum, “Pemanfaatan Kitosan Dari Cangkang Bekicot (*Achatina fulica*) Sebagai Pengawet Ikan Kembung (*Rastrelliger sp*) dan Ikan Lele (*Clarias batrachus*),” *J. Tek. Kim. USU*, 2015, doi: 10.32734/jtk.v3i4.1656.
- [5] M. Kurniasih and D. Kartika, “Sintesis dan karakterisasi fisika-kimia kitosan,” *J. Inov.*, 2011.
- [6] S. Agustina, I. Swantara, and I. Suartha, “Isolasi Kitin, Karakterisasi, dan Sintesis Kitosan dari Kulit Udang,” *J. Kim.*, 2015.
- [7] N. Morin-Crini, E. Lichtfouse, G. Torri, and G. Crini, “Applications of chitosan in food, pharmaceuticals, medicine, cosmetics, agriculture, textiles, pulp and paper, biotechnology, and environmental chemistry,” *Environmental Chemistry Letters*. 2019, doi: 10.1007/s10311-019-00904-x.
- [8] F. W. Mahatmanti and W. Sumarni, “Kajian Termodinamika Penyerapan Zat Warna Indikator Metil Oranye (MO) dalam Larutan Air oleh Adsorben Kitosan,” *J. Kim. Sains dan Apl.*, 2003, doi: 10.14710/jksa.6.2.13-18.
- [9] F. Widhi Mahatmanti, Nuryono, and Narsito, “Physical characteristics of chitosan based film modified with silica and polyethylene glycol,” *Indones. J. Chem.*, 2014, doi: 10.22146/ijc.21249.
- [10] F. Widhi Mahatmanti, Nuryono, and Narsito, “Adsorption of Ca(II), Mg(II), Zn(II), and Cd(II) on chitosan membrane blended with rice hull ash silica and polyethylene glycol,” *Indones. J. Chem.*, 2016, doi: 10.22146/ijc.21176.
- [11] E. J. Dompeipen, M. Kaimudin, R. P. Dewa Balai Riset dan Standarisasi Industri Ambon, J. Cengkeh, and B. Merah Ambon, “Isolasi Kitin Dan Kitosan Dari Limbah Kulit Udang,” *Majalah BIAM*, 2016.
- [12] E. J. Dompeipen, M. Kaimudin, R. P. Dewa Balai Riset dan Standarisasi Industri Ambon, J. Cengkeh, and B. Merah Ambon, “Isolasi Kitin Dan Kitosan Dari Limbah Kulit Udang Isolation of Chitin and Chitosan From Waste of Skin Shrimp,” *Maj. BIAM*, 2016.
- [13] M. F. J. D. P. Tanasale, A. Killay, and M. S. Laratmase, “Kitosan dari Limbah Kulit Kepiting Rajungan (*Portunus sanguinolentus* L.) sebagai Adsorben Zat Warna Biru Metilena,” *J. Natur Indones.*, 2012, doi: 10.31258/jnat.14.1.165-171.
- [14] A. Saleh, S. A. Mukhtar, M. Fawwaz, M. Pratama, R. Kosman, and T. Naid, “Deacetylation degree of chitosan by various bases and its metal adsorption ability related on antioxidant activity,” *J. Chem. Pharm. Res.*, 2015.
- [15] Z. Z. Zam, S. Umar, T. Robo, and F. Muin, “Isolation and Characterization of Chitosan from Coconut Crab Skin Origin of Halmahera Island with Ftir,” no. Ictl 2018, pp. 298–302, 2020, doi: 10.5220/0008901202980302.
- [16] S. Bahri, E. A. Rahim, and S. Syarifuddin, “Derajat Deasetilasi Kitosan Dari Cangkang Kerang Darah Dengan Penambahan Naoh Secara Bertahap,” *Kovalen*, 2015, doi: 10.22487/J24775398.2015.v1.i1.5161.
- [17] N. Rokhati, “Pengaruh Derajat Deasetilasi Khitosan Dari Kulit Udang Terhadap Aplikasinya Sebagai Pengawet Makanan,” *Reaktor*, 2012, doi: 10.14710/reaktor.10.2.54-58.
- [18] S. Bahri and E. Abd Rahim, “Derajat Deasetilasi Kitosan Dari Cangkang Kerang Darah Dengan Penambahan Naoh Secara Bertahap [Chitosan Deacetylation Degree from *Anadara granosa* by Gradually Adding NaOH],” *Kovalen*, 2015.
- [19] M. M. Drew, S. Harzsch, M. Stensmyr, S. Erland, and B. S. Hansson, “A review of the biology and ecology of the Robber Crab, *Birgus latro* (Linnaeus, 1767) (Anomura: Coenobitidae),” *Zoologischer Anzeiger*. 2010, doi: 10.1016/j.jcz.2010.03.001.
- [20] M. E. Laidre, “Coconut crabs,” *Current Biology*. 2018, doi: 10.1016/j.cub.2017.11.017.
- [21] W. J. Fletcher, I. W. Brown, and D. R. Fielder, “Growth of the coconut crab *Birgus latro* in Vanuatu,” *J. Exp. Mar. Bio. Ecol.*, 1990, doi: 10.1016/0022-0981(90)90158-9.
- [22] A. Nugroho CS, N. Dwi Nurhayati, and B. Utami, “Sintesis Dan Karakterisasi Membran Kitosan Untuk Aplikasi Sensor Deteksi Logam Berat,” *Molekul*, 2011, doi: 10.20884/1.jm.2011.6.2.100.
- [23] M. Shell, “Extraction and Characterisation of Chitin and Chitosan from,” □□□□□ 2013, □□□□□□□□.
- [24] S. Kumari, P. Rath, A. Sri Hari Kumar, and T. N. Tiwari, “Extraction and characterization of

- chitin and chitosan from fishery waste by chemical method,” *Environ. Technol. Innov.*, 2015, doi: 10.1016/j.eti.2015.01.002.
- [25] K. Baysal, A. Z. Aroguz, Z. Adiguzel, and B. M. Baysal, “Chitosan/alginate crosslinked hydrogels: Preparation, characterization and application for cell growth purposes,” *Int. J. Biol. Macromol.*, 2013, doi: 10.1016/j.ijbiomac.2013.04.073.
- [26] C. Berthomieu and R. Hienerwadel, “Fourier transform infrared (FTIR) spectroscopy,” *Photosynthesis Research*. 2009, doi: 10.1007/s11120-009-9439-x.
- [27] M. A. Mohamed, J. Jaafar, A. F. Ismail, M. H. D. Othman, and M. A. Rahman, “Fourier Transform Infrared (FTIR) Spectroscopy,” in *Membrane Characterization*, 2017.
- [28] F. For and I. Of, “Case Study FTIR for Identification of Contamination,” *Jordi*, 2017.
- [29] S. Mukhopadhyay, “FTIR spectroscopy - principles and applications,” *J. Text. Assoc.*, 2003.
- [30] Y. X. Xu, K. M. Kim, M. A. Hanna, and D. Nag, “Chitosan-starch composite film: Preparation and characterization,” *Ind. Crops Prod.*, 2005, doi: 10.1016/j.indcrop.2004.03.002.
- [31] Q. Li, E. T. Dunn, E. W. Grandmaison, and M. F. A. Goosen, “Applications and Properties of Chitosan,” *J. Bioact. Compat. Polym.*, 1992, doi: 10.1177/088391159200700406.
- [32] Y. Dong, C. Xu, J. Wang, M. Wang, Y. Wu, and Y. Ruan, “Determination of degree of substitution for N-acylated chitosan using IR spectra,” *Sci. China, Ser. B Chem.*, 2001, doi: 10.1007/BF02879541.