PREPARATION AND CHARACTERIZATION OF GIANT TIGER SHRIMP (*Penaeus monodon)* SHELL-BASED CHITIN AS BIOCOAGULANT FOR WATER PURIFICATION

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Abstract: Giant tiger shrimp (*Penaeus monodon*) shells are solid waste that can be utilized for water purification by converting them into chitin-based biocoagulant. The extraction and deproteination of giant tiger shrimp shells (*Penaeus monodon*) resulted in 83.34% w/w, followed by a demineralization yield of 91.61% w/w product. Chitin extract was used as a biocoagulant using the Jar test method on a fixed variable of 1 L well water and the independent variables of chitin weight (mg) and stirring speed (rpm). The results showed that 15 mg/L chitin reduced the turbidity value of well water from 3.08-1.03 NTU and decreased the Total Dissolved Solids (TDS) from 555-500 mg/L, at 200 rpm and pH 8.4. In conclusion, our investigation proves that chitin derived from giant tiger shrimp shells can be used as a biocoagulant for water purification.

Keywords: Chitin; biocoagulant; giant tiger shrimp; water purification; TDS

Abstrak: Kulit udang merupakan limbah padat yang dapat digunakan untuk penjerniahan air, dengan mengonversi limbah tersebut menjadi biokoagulan berbasis *chitin*. Limbah kulit udang Windu (*Penaeus monodon)* diekstrak menjadi *chitin* sebagai bahan baku *Biokoagulan* dalam penjernihan air sumur. Proses ekstraksi kulit udang windu (*Penaeus monodon)* diperoleh rendemen sebesar 83,34% melalui proses deproteinasi, diperoleh rendemen sebanyak 91,61% melalui proses demineralisasi. Hasil ekstrak *chitin* digunakankan sebagai biokoagulan dengan metode *Jar test* pada variabel tetap sebesar 1 L air sumur dan variabel berubah adalah massa *chitin* dan waktu pengadukan. Hasil penelitian menunjukkan bahwa 15 mgram/L *chitin* mampu menurunkan nilai kekeruhan air sumur dari 3,08-1,03 (NTU) dan menurunkan *Total Dissolved Solids* TDS dari 555-500 (mg/L), dengan kecepatan rotasi 200 rpm untuk nilai pH 8,4. Kesimpulan, penelitian ini menunjukkan bahwa chitin yang diperoleh dari kulit udang windu dapat digunakan sebagai biokoagulan pada proses penjernihan air.

Kata kunci: *Chitin*; biokoagulan; konversi; kulit udang windu; penjernihan air; TDS

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Introduction

The head and shell of giant tiger shrimp (*Penaeus monodon*) are considered invaluable solid waste that has the potential of polluting the environment (Kementerian Riset, 2019). The majority of the shells are only used as a mixture of animal feed, where many are still underutilized, becoming waste in the environment. On the other hand, the shrimp shell can be converted into chitin and chitosan (Hambali, M., Wijaya, E., & Reski, 2017). Chitin is a polysaccharide with a structural component that originated mainly from the animal exoskeletons. As the water ecosystem, annually Chitin is produced from various exoskeletons (shell), such as shrimp, crab, clams, fish, and lobster, reaching 1011 tonnes per year (Pandharipande, S. L., 2016). Thus, researchers are challenged to utilize the waste product into a material with a higher economic value, including the biopolymer – chitin. Frantz et al. (2020) has converted chitin from shrimp shell waste, using green solvents, producing biocoagulant designated for surface water treatment.

The exoskeleton of a shrimp consists of chitin (Ziming Lin et al., 2021), where it is composed of cellular N-acetyl-D-glucosamine (2-acetamido-2-deoxy-D-glucopyranose) that are bound linearly with β- (1-4) bonds (figure 1). Chitin is white, dense, rigid, and containing nitrogen from the polysaccharide, used as a material for pollutant removal from water (Ziming Lin et al., 2021)

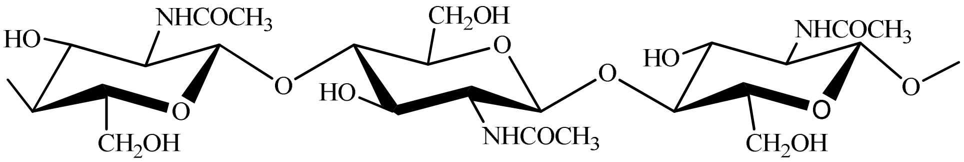

Figure 1. Chemical structure of chitin (Ziming Lin et al., 2021)

Water is a natural resource that humans are dependent on, covering 72% of the earth's surface area. The Source of abundant water in the earth is destined for humans to meet their needs, so men are forbidden to pollute the water. Polluted water may negatively impact human life as a whole. Allah has given the laws inherent in all creation, and the law works according to the *sunnatullah*, but if it is disobeyed, it will negatively impact. In accordance with the word of Allah in the Quran surah Ar-Rum verse 41:

ظَهَرَ ٱلْفَسَادُ فِى ٱلْبَرِّ وَٱلْبَحْرِ بِمَا كَسَبَتْ أَيْدِى ٱلنَّاسِ لِيُذِيقَهُم بَعْضَ ٱلَّذِى عَمِلُوا۟ لَعَلَّهُمْ يَرْجِعُونَ

Meaning: "Mischief has appeared in the land and the sea because of what the hands of the mankind have earned, that He may make them taste a part of that which they have done, so that they may return (turn to Allah)." (Al-Jazairi, 2018).

For this reason, our faith and piety should be strengthened to have more awareness regarding the preservation of the environment and sustainable management of natural resources. Well is one of the sources of surface water available for humans on earth, used for daily needs (Yang et al., 2020). Unfortunately, the surface water quality has depleted due to the rapid increase in population. To overcome, our work purposes the use of giant tiger shrimp shells for the water treatment.

Coagulation is one of the water purification techniques that works through the clumping stage of colloid particles (Ezemagu et al., 2020). Biocoagulant can be derived from the shrimp shells, including that of *Chaetoceros sp* (Teh, C.Y., Budiman, P.M., Shak, K.P.Y., 2016).

Water pollution caused the production of various wastes released from industries that have experienced exponential growth recently. In this light, the use of renewable and biodegradable materials such as chitin holds a significant role due to the increase in demand for renewable resources, which became the research focus for many. Specifically, chitin is a biocoagulant that is interested in being used for wastewater treatment (Dao, V.H., Cameron, N.R., Saito, K., Synthesis, 2016). Shrimp shell waste is one of the fundamental ingredients for chitin preparation used as a biocoagulant (Ziming Lin et al., 2021). It is believed that biocoagulant will keep gaining the spotlight and attracts many researchers due to their availability, low production cost, eco-friendliness, multifunctionality, and biodegradability (Yang, R., Li, H., Huang, M., Yang, H., Li, 2016). Our work uses the biocoagulant obtained from the giant tiger (P. monodon) shell, chitin, for purification of well water from the above explanation.

Materials and instruments

Materials used in this research were 1 L well water obtained from Darussalam District, NaOH 3% (Merck), HCl 2M (Merck), NaOCl (Merck), distilled water, Acetone (Merck).

Instruments used include laboratory glassware, pH-meter, analytical balance, oven, water bath, hot plate, Fourier Transform Infrared Spectrometer (Shimadzu IR *Prestige-21*), Jar test, crusher, and centrifuge (Hettich EB 200).

Methods

Pretreatment of shrimp shell

The shells of giant tiger shrimp (*P. monodon*) were cleaned and dried under the sunlight for ± 4 days to remove the water. Then, the sample was crushed and sifted (100 mesh).

Isolation of chitin

The conversion into chitin was conducted in three steps; deproteination, decalcination, and decolorization (Dompeipen, Edward, 2017). Deproteination was initiated by mixing the dried powdered shells with NaOH 3% and heated in a water bath for 2 h. The mixture was filtered, where the residue was neutralized with distilled water, and lastly dried for 3 h.

The decalcination was conducted by collecting the residue from the deproteination process and mixing it with HCl 2 M. The mixture was then filtered. The residue was neutralized using distilled water and dried for 3 h.

At the last step, decolorization, the residue obtained previously was mixed with NaOCl, soaked for 2 h, and the residue obtained was neutralized using distilled water.

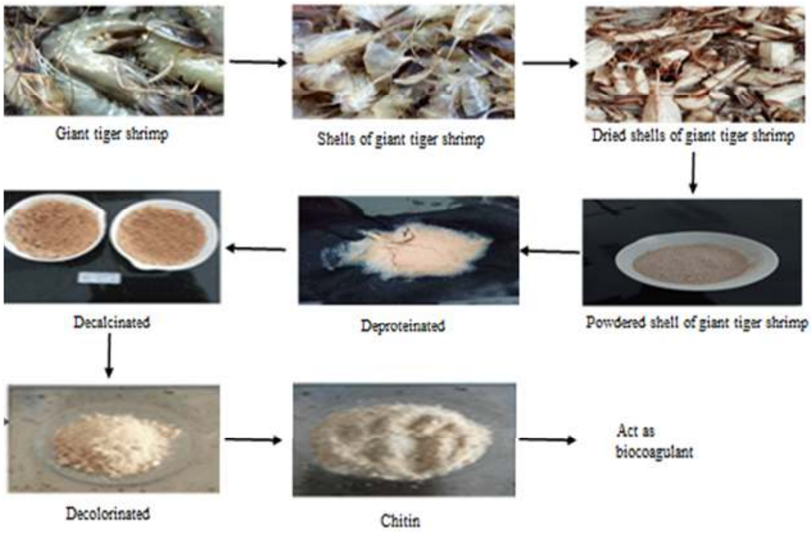

Figure 2. The conversion process of giant tiger shrimp shells into chitin

Study on the biocoagulant activities

As much as 1 L well water mixed with chitin powder (5 mg), homogenized by stirring with jar test method (Patricia et al., 2018). The method used in the application was the Jar test with the repeated experiments by changing the chitin weight and rotation speed variables according to the experimental design presented (table 1).

Table 1. Variations of biocoagulant and rotation speed (Patricia et al., 2018)

Biocoagulant weight (mg)	Rotation speed (rpm)
0	100
5	125
10	150
15	175
20	200

Results

The utilization of giant tiger shrimp (*P. monodon*) shells is a recycling process, in which theologically, the shells are waste (Sa'diyah, 2018). This report suggests the utilization of non-useful ingredients as a form of human responsibility in reducing waste. Islam has regulated the inherent mind of humans to lead them in utilizing the creation of god. Of which is the processing of useless materials, including shrimp shells. Quran states that:

وَسَخَّرَ لَكُم مَّا فِى ٱلسَّمَٰوَٰتِ وَمَا فِى ٱلْأَرْضِ جَمِيعًا مِّنْهُ ۚ إِنَّ فِى ذَٰلِكَ لَءَايَٰتٍ لِّقَوْمٍ يَتَفَكَّرُونَ

"And He has subjected to you whatever is in the heavens and whatever is on the earth - all from Him. Indeed in that are signs for a people who give thought." (Al-Jazairi, 2018)

Table 2. Data of chitin isolation results

Stage	Weight (g)	Yield (%)
Deproteination	21	83.34
Decalcification	8.82	98
Decolorization (Chitin)	8.08	91.61

Drying the shrimp shell under the sunlight for 7 days yielded 39.05 dried shells from originally 100 g. The dried shells were crushed to increase the surface area, and 25.18 g powder was obtained.

As for the deproteination, the yield reached 21 g from originally 25.18 g, and decalcination resulted in 8.82 g samples from originally 9 g processed. As for the decolorization, 8.08 g was obtained from 8.82 g feed material.

Chitin isolation resulted in an 8.08 g yield, which means the total yield was 91.61%. Chitin obtained was characterized using FT-IR to identify the contained functional groups.

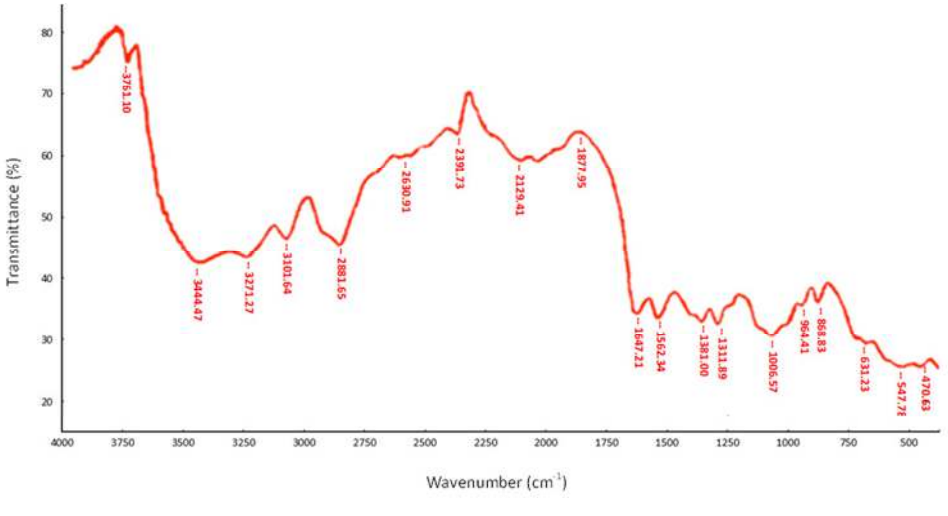

Figure 3. FT-IR spectral profile of the investigated chitin

Table 3. Characteristics of chitin structure derived from shrimp shells (Dompeipen, Edward, 2017)

Functional group	Wavenumber (cm^{-1})	
	Investigated chitin	Chitin in reference
N – H stretching	3269	3300 – 3250
OH	3442	3448
CH_3	1378	1419
N – H bending	1560	1560 – 1530
C = O stretching	1645	1680 – 1640
C – H stretching	2879	2891
N – H wagging	696	750 – 650
C – O – C	1093	1072

The FT-IR spectra of chitin show the absorbance band at 3442 cm^{-1} assigned for O-H stretching. The absorbance band represented the amide group (N-H) in chitin at 3269 cm^{-1}. The following absorbance band at 2879 cm and 1645 cm^{-1} indicate C-H aliphatic and C=O, respectively. The presence of CH_3 was observable at wavenumber 1378 cm^{-1}. Therefore, from this FT-IR analysis, we can confirm that the sample extracted from the giant tiger shrimp shell is chitin. The isolation has met the standard obtained previously (Islem, Y., Marguerite, 2015). The acetyl group ($-COCH_3$) is an indicator of chitin structure that distinguishes it from chitosan; because in chitosan, it does not contain the acetyl group ($-COCH_3$).

This research informs that the tiger shrimp shell can be used to produce biocoagulant – chitin. In its application as a biocoagulant, the investigation was carried out at room temperature (25°C) at 1 atm.

Table 4. Application of chitin as biocoagulant

Biocoagulant weight (mg)	Rotation speed (rpm)	pH	TDS (mg/L)	Δ TDS (mg/L)	Turbidity (NTU)	Δ Turbidity (NTU)
0*	100	8.2	555	0	3.08	0
	125	8.2	555	0	3.08	0
	150	8.2	555	0	3.08	0
	175	8.2	555	0	3	0.8
	200	8.2	538	17	3	0.8
5	100	8.3	538	17	3	0.8
	125	8.3	538	17	3	0.8
	150	8.3	538	17	2.08	1
	175	8.3	538	17	2.08	1
	200	8.3	538	17	2.08	1
10	100	8.4	538	17	2.08	1
	125	8.4	521	34	2	1.08
	150	8.4	538	17	2	1.08

Biocoagulant weight (mg)	Rotation speed (rpm)	pH	TDS (mg/L)	Δ TDS (mg/L)	Turbidity (NTU)	Δ Turbidity (NTU)
	175	8.4	521	34	1.59	1.49
	200	8.4	521	34	1.59	1.49
15	100	8.4	520	35	1.59	1.49
	125	8.4	520	35	1.19	1.89
	150	8.4	500	55	1.08	2
	175	8.4	500	55	1.08	2
	200	8.4	500	55	1.03	2.05
20	100	8.4	520	35	2.01	1.07
	125	8.4	520	35	2.01	1.07
	150	8.4	523	32	2.08	1
	175	8.4	525	25	2.08	1
	200	8.4	525	25	3	0.8

*Acting as a control

Discussion

pH

From table 4, the acidity (pH) had ranged between 8.3 – 8.4 for the investigation setting. It is owing to the basic property of chitin. The mineral contents in the shrimp shell include $CaCO_3$ that is basic when dissolved in water, resulting in a higher pH value in the solution (Wibowo *et al.,* 2019). In line with the research conducted by Saxena et al. (2019), a coagulant is most effective in working at pH ranging from 7.5 – 8. The pH value is still allowable for consumption based on the ministerial decree of health regarding well water (Permenkes Nomor 492/Menkes/IV/2010).

Turbidity

The turbidity of the well water treated using biocoagulant chitin experienced a decrease. Based on our investigation, the turbidity ranged from 3.08 – 1.03. The lowest turbidity was achieved with the addition of a biocoagulant of as much as 15 mg. It is due to the maximum limit of coagulants used. In this study, the addition of biocoagulant reached the limit where the optimum weight was obtained at 15 mg with the rotation speed of 200 rpm. At 20 mg, the biocoagulant yielded higher turbidity attributed to the overwhelming presence of cations in the water acting as colloidal particles. Positive charges with repelling one another led to deflocculation (Hendrawati, Susi Sumarni, 2016). This reaction caused the water to be more turbid. The flocculation itself was ascribed to the adsorptive mechanism (Dompeipen, Edward, 2017). It is within the same agreement with Pratama, A, (2016), where the addition has the maximum limit; further addition of biocoagulant results in excessive cations preventing the floc formation. Based on the ministerial decree of health No. 492/Menkes/IV/2010, the turbidity level was still considered allowable (< 5 NTU).

TDS

Total Dissolved Solids (TDS) is the amount of dissolved organic or inorganic solids (Teh, C.Y., Budiman, P.M., Shak, K.P.Y., 2016). In table 4, it is shown that the TDS level of well water with the optimum weight of biocoagulant (15 mg; 150-200 rpm) is the lowest, with the reduction, reached 55 mg/L. This may be attributed to the neutralization of electrical charge present on the colloidal particles of the well water (Hendrawati, Susi Sumarni, 2016). In this study, the addition of chitin as much as 20 mg increasing TDS, associated with the leaching of minerals, originated from the chitin itself. The minerals dissolved into the well water forming positive charges, which eventually caused the increase in TDS (Wibowo et al., 2019).

A study by Patricia *et al.* (2018) in water purification using chitin derived from oyster mushroom achieved the best combination at 1000 mg/L biocoagulant with a rotation speed of 100 rpm. Their research required a higher amount of chitin to achieve the optimum purification result than ours using giant tiger shrimp shells.

Water purification by biocoagulant is a process of agglomeration of turbidity, causing particles or colloids that cannot be removed by simple gravitation. Biocoagulant may destabilize the colloid that neutralize the electrical charges of the colloid surface. It leads to the formation of colloidal floc with bigger size particles leading to precipitation. According to Ezemagu et al. (2020), coagulation is the neutralization of negatively charged particles (causing the turbidity) with the help of positively charged particles (biocoagulant). It further leads to the aggregation of colloidal particles by the presence of Van der Waals attraction. Based on the research (Ezemagu et al., 2020), the treatment of wastewater using mucuna seed as biocoagulant, the optimal condition was obtained at 2 g/L. In comparison with ours, their research required a higher amount of biocoagulant.

Based on these results, chitin obtained in our study can be utilized as a biocoagulant, giving the information that the giant tiger shrimp shell (*P. monodon*) can produce chitin biocoagulant, which is capable of reducing the turbidity and TDS in well water.

Conclusion

The giant tiger shrimp (*P. monodon*) can be extracted to produce chitin which can be utilized as a biocoagulant. In its application, chitin significantly reduced the turbidity with the optimum weight of 15 mg/L at 200 rpm. The TDS was reduced at the optimal weight of 15 mg/L with a rotation speed of 200 rpm. As for pH value, the variation did not affect observably against the reduction of turbidity and TDS after the addition of biocoagulant chitin.

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