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Producing chitosan from shellfish waste and its application as a natural coagulant in water purifiers

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ARTICLE INFO

Article history:
Received: 07 July 2024
Received in revised form: 28 October 2024
Accepted: 01 November 2024

Keywords:
Pyrite, pigment, inorganic, mineral, activation

ABSTRACT

Waste from simping shellfish (*Amusium pleuronectes*) shells can pose environmental hazards if waste levels exceed the threshold. This research aims to produce chitosan from shellfish, specifically simping shells, for the purification of raw water. The optimal dosage for both chitosan and alum coagulants in water samples with bay river turbidity (49.5 NTU) is 1 ppm, resulting in a turbidity removal percentage of 99%. The optimum pH for chitosan coagulant (1 ppm) is 6.32, and for alum coagulant (1 ppm) is 8. For bay river water with an initial turbidity of 49.5 NTU, the optimal dose of chitosan coagulant is 1 ppm, achieving a turbidity removal percentage of 99%. Producing chitosan from shellfish waste as a natural coagulant for water purification offers an eco-friendly, cost-effective solution that enhances water quality, reduces seafood industry waste, and provides a safe alternative to chemical coagulants, with potential applications in various fields.

1. Introduction

The production of drinking water from raw water sources requires several stages of processing, including coagulation and flocculation, which removes turbidity in the form of suspended and colloidal material. Research on the coagulation process is commonly conducted, and several types of coagulants have been tested for their efficacy and efficiency in this process. Synthetic coagulants are used more often in water purification processes because they are easier to get and are worth it from an economic point of view. However, overuse of synthetic coagulants will actually have bad effects on the environment and health because this type of coagulant is hard to biodegradable.

Chitosan can function as a more effective coagulant than alum, as evidenced by its ability to reduce water turbidity even at low concentrations." This version maintains the clarity while slightly restructuring the sentence for flow [29].

Chitosan has several benefits when used as a coagulant, including non-toxicity, easy biodegradability, polyelectronic properties, and easy interaction with other organic materials like proteins. It is therefore hoped that the coagulant made from the natural substance chitosan will have a high added value and be environmentally benign.

The second most abundant polysaccharide on Earth after cellulose, chitin is the precursor of chitosan and is formed through deacetylation. It is present in the cell walls of certain fungi and the skeletons of invertebrates. Chitosan is a cationic polyelectrolyte derived from organic materials that may be utilized as a natural coagulant in water treatment procedures [5].

This research aims to produce chitosan from shellfish, specifically simping shells, for the purification of raw water. The results of this research are then utilized for purifying raw water. An analysis was conducted to examine the impact of chitosan, a natural coagulant derived from simping shell waste, on the purification process. This analysis focused on parameters such as pH, turbidity, and Total Suspended Solids (TSS).

The characteristics of chitosan resulting from this research (research chitosan) were compared to those of commercial chitosan. The purification results of these two types of chitosan were then compared to those obtained with alum. Characteristics including functional group content and degree of deacetylation (DD) were analyzed using Fourier Transform Infrared Spectroscopy (FTIR).

2. Materials and Methods

2.1. Materials

The tools used in this research include a 100 mL measuring flask, 1000 mL beaker, blender, 10 mL measuring pipette, spatula, analytical balance, litmus paper, thermometer, 100 mesh sieve, turbidity meter, test jar, glass funnel, filter paper, aluminum foil, desiccator, oven, and hot plate.

The materials for this research are simping shell waste obtained from the beach, distilled water, 6% and 50% NaOH

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http://dx.doi.org/10.20527/k.v13i2.19882

solutions, 1 N HCl, 1% acetic acid, and 1% alum solution, which are used for comparisons. The water samples came from Betung Bay river water in Lampung, Indonesia. The research comprised the following main stages: producing chitosan from shellfish, dissolving chitosan, chitosan characteristics analysis, water sampling, and purification tests.

2.2. Making chitosan

Making chitosan from shellfish waste involves the process of demineralization, deproteination, and deacetylation [34]. Demineralization is carried out by soaking the shrimp shells in 1 N HCl. The shrimp shell/HCl ratio is 1:10 (w/v). This mixture is heated at 80°C for 1 hour while stirring. Deproteination is performed by soaking the demineralized shellfish in 6% NaOH and then in 50% NaOH, with a ratio of 1:10 (w/v). This mixture is heated at a temperature of 110°C for 2 hours while stirring. Deacetylation, the conversion of chitin to chitosan, occurs by immersing deproteinized shellfish in acetic acid, with a ratio of 1:10 (w/v). This solution is heated at a temperature of 110°C for 2 hours, stirring continuously. After each step of the process, the mixture is cooled for 30 minutes and then filtered. The solids collected on the filter cloth are washed with distilled water until the pH becomes neutral. Subsequently, the shells are dried in an oven at 80°C for 12 hours and then weighed.

2.3. Chitosan solution

1 gram of chitosan powder from clam shells was then dissolved in 100 mL of 1% acetic acid to make a 1% chitosan solution. Next, the chitosan solution was used to purify 500 mL of sample water. The dose of chitosan for clarification was varied from 1 ppm to 6 ppm.

2.4. Chitosan characterization with FTIR

Characterization of chitosan using a Shimadzu brand FTIR spectrometer. The degree of deacetylation (DD) shows the number of free amine groups in the chitosan polysaccharide. The DD value of chitosan can be seen from the FTIR spectrum by calculating the percent transmittance at a certain wave number. DD is determined to find out how much chitin has been converted into chitosan.

The DD calculation follows equation (1) below.

$$\%DD = \left(1 - \frac{A1655}{A3450}\right) \quad (1)$$

with:

DD = Degree of Deacetylation (%)
(A1665) Amida = at 1655 cm' in the amide band
= %T
(A3450) Hidroksil = at 3450 cm' in the hydroxyl band

2.5. Water samples

Water samples were taken from the Teluk River, totaling 30 L (3 buckets @ 10 L each). Water sampling followed the grab sampling method. These changes make the sentence clearer by specifying that each bucket contained 10 liters of water and by adjusting the phrasing slightly for consistency.

2.6. Turbidity testing with jar test

The jar test aims to determine the correct coagulant dose. The jar test process follows the procedure guide used at the University of Lampung. The jar test experiment was conducted with varying chitosan doses of 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, and 6 ppm. 500 mL of raw water was filled into each beaker.

The jar test apparatus was operated at 140 rpm for 5 minutes (fast stirring), followed by 30 rpm for 10 minutes (slow stirring). Subsequently, the jar test apparatus was left undisturbed for 20 minutes for the flocculation process. Turbidity levels before and after the jar test were measured using a turbidity meter.

The coagulant dosage and percentage of turbidity reduction are calculated from the percentage of turbidity reduction using equations (2) and (3).

Thepercentage of turbidity reduction using equations (2) and (3).

$$\text{Dosage} = \frac{\text{Coagulant Conc.(ppm)} x \text{ Vol.sample (mL)}}{1000 \text{ mg/L}} \quad (2)$$

$$\text{Percentage reduction in turbidity} = \frac{A-B}{B} \text{x } 100\% \quad (3)$$

with:

A= Initial turbidity value before adding coagulant
B = Final turbidity value after adding coagulant

2.4. TSS measurement

Analysis of TSS (Total Suspended Solid) values using the gravimetric method based on SNI 6989.3:2019 regarding how to test TSS suspended solids gravimetrically. Calculation of the TSS value uses equation (4).

$$\text{TSS (mg/L)} = \frac{(B-A) x\ 1000}{volume\ sampel\ (mL)} \quad (4)$$

With:
A = Weight of filter paper + dry residue (mg)
B = Weight of filter paper (mg)

3. Results and Discussion

3.1. Chitosan production results

After drying, 800 grams of clam shells were ground using a blender, then sieved using a 100-mesh sieve. This research resulted in a decrease in mass, from 800 grams to 25.5 grams of clam shell powder. The demineralization and deproteination process produced 19.26 grams of chitin. The next process of deacetylation produced 17.14 grams of chitosan. The mass balance results of this research were compared with the literature data and are presented in Table 1.

Table 1. The crystallite size of the treated pigment

Clam shell (g)	chitin (g)	chitosan (g)	Yield (%)	Ref
70 grams	17.32	16.64	23.7	[22]
100 grams	22.12	18.24	18.2	[23]
800 grams	19.26	17.14	21.4	This Research
18,17 (shrimp shell)	8.71	5.80	31.9	[29]

If calculated from shellfish powder, the yield in this study is slightly greater than in other studies. The difference in yield may be attributed to the use of shellfish as raw material in

powdered form, which facilitates better mass transfer. Variations in shellfish types and differences in the chitosan manufacturing process can also affect the yield of chitosan. Additionally, material loss may occur due to the loss of polymer mass during deacetylation and chitosan particles during washing.

3.2. Chitosan characterization using FTIR

The FTIR spectrum results of research chitosan (from this study) and commercial chitosan are presented in Figure 1. The chitosan from this study is similar to commercial chitosan. Both contain a hydroxyl group (OH) at a wave number of 3235 cm^{-1}, alkane (C-H) at a wave number of 2877 cm^{-1}, amine (NH_2) at a wave number of 1580 cm^{-1}, and C-O at a wave number of 1021 cm^{-1}. The characterization results are also presented in Table 2. The structure of the chitosan molecule and the position of each functional group are shown in Figure 2.

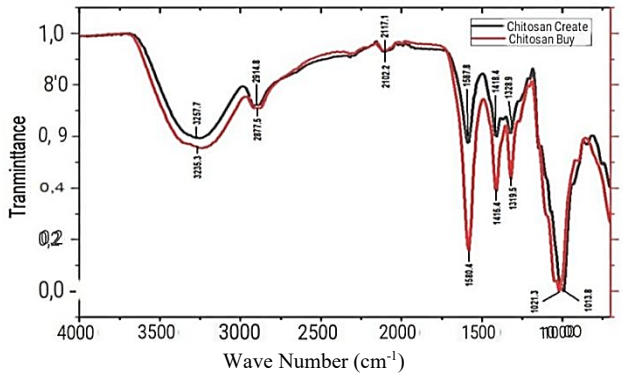

Fig. 1. FTIR test results for research chitosan (black line) and commercial chitosan (red line)

Table 2. FTIR Characterization Results

Bond	Functinal groups	Wave number (cm^{-1})	
		Research chitosan	Commercial chitosan
O-H	Hydroxyl	3257.7	3235.3
C-H	Alkanes	2914.8	2877.5
NH2	Amine	1587.8	1580.4
C-O	C-O	1013.8	1021.3

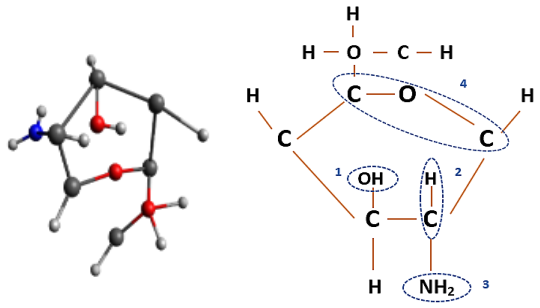

Fig. 2. The structure of the chitosan molecule and the position of its functional groups

3.3. Comparison of DD research chitosan and commercial chitosan

The degree of deacetylation (DD) is defined as a parameter for the release of acetyl groups from chitin. The degree of deacetylation is an important parameter that influences chitosan properties such as solubility, chemical reactivity, and ease of biodegradation. A comparison of the characteristics of research chitosan and commercial chitosan is presented in Table 3. Each chitosan shows almost the same DD values: they are soluble in acetic acid, have a powdery texture, and odorless.

Table 3. Physical Properties of Research Chitosan and Commercial Chitosan

Parameters	Chitosan Research	Commercial Chitosan
Solubility in Acetate acids	Late	Late
Texture	Powder	Powder
Color	White	White
Smell	Odorless	Odorless
Degree of deacetylation	82.42%	82.38%
Mesh	100	100
Picture		

The degree of deacetylation in research chitosan (82.42%) is slightly different from commercial chitosan (82.38%). The particle size of the raw material may result in differences in the degree of deacetylation. The value of the degree of chitosan deacetylation is determined by several factors, namely NaOH concentration, temperature, and the duration of the deacetylation process. A high concentration of NaOH will result in a faster reaction rate, leading to the production of higher OH groups and the release of higher CH_3COO groups. Consequently, there will be more amine groups in chitosan. Reaction time also causes chitosan degradation, characterized by a decrease in viscosity. The chitosan becomes more reactive as the degree of deacetylation increases because the chitosan molecular chain contains more amine groups [19].

3.4 Characteristics of river water

The water sample used was from Betung Bay river water. The turbidity and TSS values of the river water are presented in Table 4. It is evident that Betung Bay river water, Lampung is not suitable for use as clean water.

Table 4. Initial Test Results for Turbidity and TSS

Parameter	Unit	Initial Examination Results	Clean Water Quality Standards
Turbidity	NTU	49.5	5
pH	-	7.2	6.5-7.5
TSS	mg/l	74	50

3.5. Turbidity reduction

Starting from the initial turbidity value of 49.5 NTU in river water (Table 4), coagulation with research chitosan and commercial chitosan can significantly reduce turbidity. Chitosan dose of 1 ppm, water turbidity can meet the quality standards set by Minister of Health Regulation No. 492, 2010. Both research chitosan and commercial chitosan have the same effect on reducing turbidity [10].

The use of alum, which is commonly employed in previous research, exhibits an opposite tendency, namely, increasing the alum dose reduces turbidity. Alum is typically

utilized at a dosage of 20 ppm to achieve turbidity levels compliant with the quality standards outlined in Minister of Health Regulation No. 492 of 2010. The optimal alum concentration reported by other researchers ranges from 10 to 20 ppm [13]. In this study, the coagulant dose was observed only up to 6 ppm. Naturally, the percentage reduction in turbidity follows the inverse of the turbidity value: as turbidity decreases, the percentage decrease in turbidity becomes higher (Figure 3 (a) (b)).

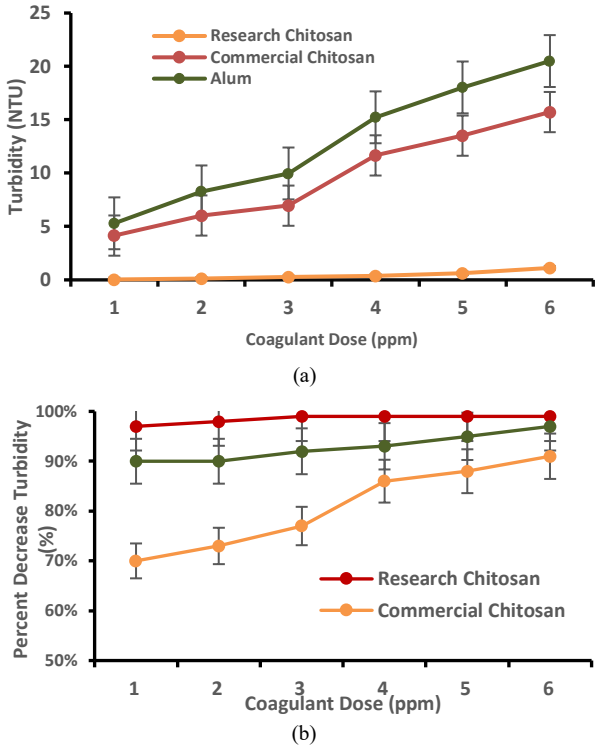

Fig. 3. The effect of coagulant dosage on (a) Turbidity value and (b) percent decrease in turbidity

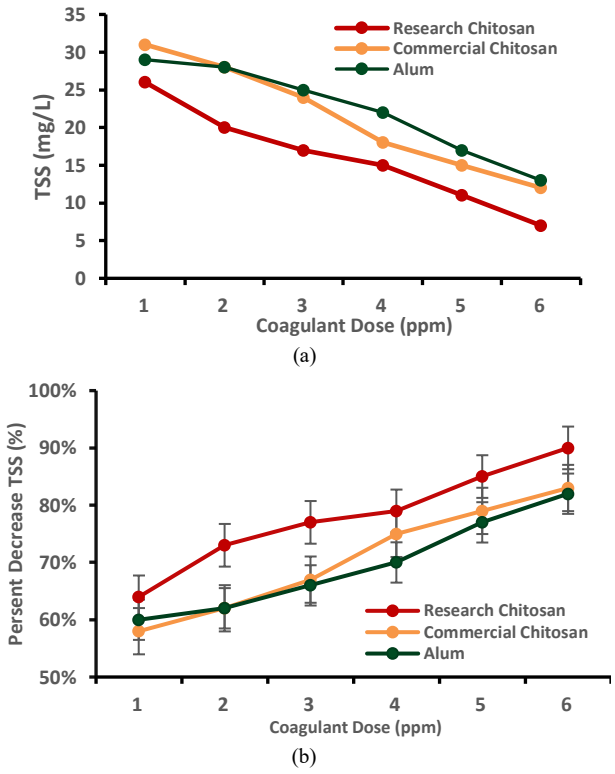

Fig. 4. Effect of coagulant dose on (a) TSS and (b) percent decrease in TSS

The TSS value in the raw water before adding coagulants was 74 mg/L (Table 4). The addition of research chitosan at doses ranging from 1 to 6 ppm resulted in a decrease in TSS. By adding chitosan at a dose of only 1 ppm, the TSS value fell to 26 mg/L, significantly below the quality standard of 50 mg/L. However, further addition of chitosan dose apparently increased the TSS value again (as shown in Figure 4), indicating possible flocculation.

Further observations showed that an increase in the dose of alum resulted in a decrease in the value of TSS. However, to achieve the quality standard for TSS value, a higher dose of alum is required than the dose used initially.

The effectiveness of clam shell chitosan coagulant in reducing TSS concentration is also supported by the research of Sinardi et al. [26]. In their study, bio-coagulants derived from clam shells were used. The required dose is relatively high: achieving a decrease in TSS value from 96 mg/L to 54 mg/L requires a coagulant dose from clam shells of 100 mg/L. The percent decrease in TSS value with coagulants made from crab shells is approximately 78%, while the percent decrease in TSS value from this study reached 87%.

3.7. Research cost analysis

The price can be estimated to be IDR 20,000 based on a base of 10 kg of shrimp skin. Processing it into chitosan requires (i) 3.65 L HCl 1N (price IDR 100,000/L) and 30 kg NaOH (price IDR 50,000/kg) [23]. Thus, in simple terms, the price of research chitosan (the result of this study) is IDR 590,409/kg, while the price of commercial chitosan is IDR 625,000/kg [20]. The production cost of research chitosan is slightly cheaper than the price of commercial chitosan. A comparison of the procurement costs of research chitosan, commercial chitosan and alum coagulants was compiled for clean water treatment capacity [16]. The high cost of producing chitosan is due to the use of chemicals in laboratory research. But keep in mind that chitosan is non-toxic and can help solve waste problems, as well as increase the added value of clamshell and crab shells [3].

The cost of research chitosan production operations may be reduced by developing the following process.

1. The use of alternative chemicals. HCl chemicals in the demineralization process (price IDR 100,000/L) can be replaced with acetic acid (price IDR 58,000/L) and while NaOH chemicals in the deproteinization process (price IDR 50,000/kg) can be replaced with $Ca(OH)_2$ (price IDR 10,000/kg) [20]. The replacement of chemicals used is due to having almost the same acidic or alkaline properties. However, the replacement of these chemicals can result in a longer processing process and lower yields [1].
2. Grinding shrimp skin into a finer powder so that the process of demineralization, deproteinization and deacetylation can take place faster, homogeneous and efficient. Chitosan in the form of a fine powder will also help speed up the drying process, and the contact surface area will be larger. So that the processes in making chitosan will also be better [8,28].

4. Conclusion

The chitosan coagulant from this study was tested to have the same characteristics as commercial chitosan, in terms of functional group composition and degree of deacetylation. The use of chitosan from this study can purify and reduce TSS levels of raw water at a dose of 1-6 ppm. By adding chitosan at

a dose of only 1 ppm, the TSS value fell to 26 mg/L, significantly below the quality standard of 50 mg/L. Meanwhile, the use of alum as a comparison in this study requires a higher dose. The bio-coagulant production process from clam shells needs to be developed so that the cost of bio-coagulant production can decrease. Researchers can explore the use of other types of river water and other types of coagulants in the process of river water purification treatment.

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