Synthesis of chitosan-CuO composite and its application as heavy metal adsorbent

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Abstract. Shrimp shells is one of the alternative sources for the potential production of chitosan. Chitosan from shrimp shells extracted with acid has high extraction results. The chitosan obtained forms composite with CuO material (mixing materials). The study investigated the synthesis, characterization, and application of chitosan from shrimp shells and the ability of chitosan-CuO composites as heavy metal adsorbent. The physical characterisation its similarity with the commercial chitosan. The composite was made by mixing chitosan and CuO. The bond formation between chitosan-CuO showed by analysis of FTIR. Absorption of chitosan-CuO to mercury (Hg) was 87%. Chitosan-CuO is very potential as absorbent of heavy metal.

1. Introduction
The use of economically valuable shrimp shell waste is to change the shell of shrimp into chitin-chitosan. The shrimp shell is waste of shrimp meat consumption. Shrimp skin waste consists of three main components; protein (25% - 44%), calcium carbonate (45% -50%), and chitin (15% - 20%) [1]. Chitin is synthesized by an enormous number of living organisms, and considering the amount of chitin produced annually in the world, it is the most abundant polymer after cellulose [2]. Content of Chitin in the waste of shrimp skin is around 20-50% dry weight. Chitin polymers are composed by monomer monomers; 2-acetamide-2-deoxy-D-Glucose (N-acetyl glucosamine) [2]. The bond between chitin monomers is the glycoside bond in the β-(1-4) position. The structure of chitin molecules is a long straight chain. Chitin is the most abundant natural polymer in the world after cellulose [3]. Chitin extract can be obtained through three stages namely the deproteinisation, demineralization and then conversion to chitosan through a deacetylation process.

Chitosan is a biopolymer derived from the processing of chitin [4]. Chitosan [poly-2-amino-2-deoxy-β-(1-4)-D-glucopiranose)] is a polyaminosaccharide compound synthesized by partially removing 2-acetyl groups from chitin [poly(2-acetamido-2 -deoxy-β- (1-4) -Dglukopiranosa)], linear biopolymers with 2000- 5000 monomer units, intertwined with β- (1-4) glycosidic bonds. Chitosan (C₆H₁₁NO₄)n is a yellowish white amorphous solid, polyelectrolyte. Its biocompatible and easy be made various composite [5]. Generally soluble in organic acids, its pH is around 4–6.5, insoluble at lower or higher pH. Solubility is influenced by molecular weight and degree of deacetylation [6]. The quality of chitosan that has been made can be determined by knowing the degree of deacetylation [7]. Chitosan has the characteristics of chemical physics, chemical stability, high reactivity, high chelation properties, and high selectivity to pollutants [8]. Chitosan has a high deacetylation and molecular weight (BM) of
84.20% and 893,000. Chitosan can form complexes (chelate) with heavy metal ions and transition metal ions especially Cu$^{2+}$, Ni$^{2+}$ and Hg$^{2+}$, but not with alkali and alkaline earth metal ions. Chitosan is considered as a precious organic biocomponent polymer because of its nontoxicity and biodegradability [9][10]. The highest adsorption capacity was achieved for chitosan powder because of the high accessible surface for metals (4). Chitosan for heavy metal removal appears to be technically feasible, and eco-friendly with very high efficacy [11].

The nature of the chitosan has the potential to be used as an absorbent material for heavy metals. The adsorption capabilities of Chitosan are because of its electrophoretic nature (NH$_3^+$) and ability to provide a site for adsorbing metal or dye molecules through the interaction of electrostatic interactions and chelation [12]. Heavy metal is a toxic metal that is dangerous if it enters the body beyond its threshold. Heavy metals have negative effects on the life of living things such as disturbing chemical reactions and inhibiting the absorption of essential nutrients [13]. Hence, it is important to decontaminate or minimize these heavy metals from the environment. Many materials that can be composited with chitosan to optimize absorption capacity such as chitosan-g-poly composite (acrylic acid-co-acrylamide) which can adsorb Copper cobalt metal, nickel and lead ions were adsorbed onto the adsorbents very rapidly within the first 120 min [14]. Composite chitosan Cu(OH)$_2$ and CuO are also able to absorb metals with uptake of up to 95% [15]. The use of chitosan as an adsorbent/biosorbent in various types of water pollutants is also quite good in the management of industrial waste because of the amino content and hydroxyl functional group, which makes it effective compared to activated carbon. Toxic metals can be distinguished from other pollutants since they are not biodegradable and can be accumulated in nature [16]. The chitosan / Cu (OH)$_2$ and chitosan/CuO sorbents were tested for the treatment of a real industrial effluent from a pesticide factory containing arsenic, copper, lead, boron and mercury. This means that these sorbents are very efficient and selective for the treatment of hazardous metals. Chitosan / CuO and chitosan/Cu(OH)$_2$ sorbents have the highest sorption capacities among selected sorbents [17]. Chitosan/CuO composites eco-friendly technique [18]. This study aims to produce chitin and chitosan compounds from shrimp shells and conduct chitosan characterization. The chitosan that has been obtained will be composited with CuO as a heavy metal adsorbent.

2 Material and Methods

Material

The main ingredients used were shrimp shells obtained from PT Wahyu Pradana Bina Mulia, Makassar Industrial Area, South Sulawesi. Other ingredients were hydrochloric acid (HCl) 1 M, 2% acetic acid, nitric acid (HNO$_3$), sterile aquabidest, 1 M sodium hydroxide (NaOH) 2M and 60%.

Tool

Glassware (Erlenmeyer, beaker, pumpkin measuring), FTIR Spectrophotometer (Fourier Transform Infrared) thermo scientific nicolet i10, Variant atomic absorption spectrophotometer (AAS) 240, column chromatography, analytic balance, oven memmart, shieve shaker, evaporator, desiccator, magnetic stairet.

Work procedures

2.1 Sample Preparation

The shrimp shell waste was dried using sunlight and then mashed and sifted to 100 mesh before being dried in an oven at a temperature of 40-50°C for 4 hours.

2.2 Chitosan Synthesis (Khairuni, 2017)

The process of making chitosan was began with the demineralization process with 1 M HCl, deproteination with NaOH 1 M, and deacetylation with 60% NaOH.
Demineralization
The shrimp shell powder was added with 1 M HCl solution with a ratio of 1: 7 (b/v). The mixture was heated at a temperature of 25-30°C for 2 hours while being stirred. The solid obtained was washed with distilled water to remove the remaining HCl. Then the solid was dried at 80°C for 24 hours, resulting in shrimp skin powder without minerals.

Deproteination
The shrimp shell powder was obtained from demineralization added with 1 M NaOH solution. The mixture was heated at 80°C for 1 hour and stirred. Then the solid was filtered and neutralized so that chitin solids were obtained. The solid obtained was dried at 80°C for 11 hours.

Deacetylation
The results obtained from the deproteination process were then passed through by deacetylation by adding 60% NaOH. The mixture was stirred and heated at 80°C for 1 hour with stirring speed. The solid obtained was neutralized to neutral pH. The solid was dried at 80°C for 24 hours.

2.3 Chitosan Characterization

Rendemen
Chitosan yield was determined based on the presentation of the weight of chitosan produced on the weight of the raw material of the shrimp shell before processed.

\[ \text{% yield} = \left( \frac{\text{kit weight produced}}{\text{initial weight}} \right) \times 100\% \]

Water content
A total of 0.3 g of chitosan was inserted into a porcelain dish which weight had been known, then dried at 105°C for 4 hours. It was then cooled in the desiccator for 30 minutes and weighed. Reheat in the oven, it was cooled in the desiccator and this was repeat until a constant weight was obtained.

Chitosan solubility
Chitosan was dissolved in glacial acetic acid with a concentration of 2% with a ratio of 1: 100 (g/mL).

Degree of Deacetylation
Chitosan was then analyzed using FTIR to determine the degree of deacetylation (DD). To determine the degree of deacetylation (DD), the base line method proposed by Domszy and Rovert was used.

\[ \text{Deacetylation degree} = 100 - \left( \frac{A1655}{A3450} \right) \times 100 \]

2.4 Making Chitosan-CuO

Chitosan solution was put into a beaker, then added with a solution of Cu(NO₃)₂ 0.5 M with a ratio of 2: 1 (40 gr / 20 mL) until a thick solution was obtained. NaOH 2 M solution was dropped in a thick solution with stirring speed until black granules were formed. Furthermore, it was left to stand for 1 night, then filtered washed with distilled water and dried. Characterization used FTIR spectrophotometer.

2.5 Metals Adsorption Process (Hg) with Chitosan-CuO

As much as 25 mL of bleach cream (X) after being destroyed was put into a column containing 1 g of chitosan-CuO and left to stand. The column lid was then opened and be accommodated with vial bottles (duplo). Furthermore, metal mercury (Hg) was analyzed using an atomic absorption spectrophotometer (AAS).

3 Results and Discussion

Chitosan
Shrimp shells are waste consumption of shrimp meat and have many applications. The shrimp shell obtained was as much as 400 gr. Shrimp shell powder will go through the process of demineralization, deproteination and deacetylation to make chitosan. The demineralization stage, which is the stage of...
removal of minerals in shrimp shells, which are mostly CaCO_3 and Ca_3(PO)_4 in coarse chitin, results in fresh powder of mineral-free shrimp. The shell of the shrimp will react with HCl so that the mineral separation is indicated by the formation of CO_2 gas in the form of air bubbles when HCl is added, so that the addition of HCl into the sample is carried out gradually so the sample does not overflow (19).

\[
\text{CaCO}_3(s) + 2\text{HCl}_{(aq)} \rightarrow \text{CaCl}_2_{(aq)} + \text{H}_2\text{CO}_3(g)
\]

\[
\text{H}_2\text{CO}_3(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}_{(l)}
\]

The deproteinization process is to remove protein that is contained in the shell of the shrimp. Chitin powder obtained was 113.2 gr. Isolation with the demineralization-deproteinization sequence yielded more yield compared to the isolation phase of deproteinization-demineralization. This is because minerals form a shield (protector) that is hard on the skin of shrimp, so that by removing minerals first it will facilitate the process of removing protein so that the % of the chitin yield is greater. Deproteination powder obtained 113.2 gr.

The process that occurs during deproteination namely NaOH will enter into the cracks of the shrimp skin to break the bonds of protein and chitin. The Na^+ ion from NaOH will bind the ends of the negatively charged protein chain. The bond protein will be extracted and is in the form of Na-proteinate which is then carried along with distilled water during washing [20]. The deacetylation process is to remove an acetyl group (NHOCH_3) into an amine group (NH_2). The chitosan powder obtained was 65.9 gr. The transformation of chitin into chitosan is through the deacetylation process. It is the process of removing acetyl groups (-COCH_3) from chitin using an alkaline solution to change to an amine group (-NH_2). Termination of the bond between the acetyl group and the nitrogen group takes place so that it changes into an amine group (-NH_2) needs to be used sodium hydroxide with a concentration of 60%.

![Figure 1 Deacetylation of chitin into chitosan (Rahayu and Purnavita, 2017)](image)

Characterization of chitosan carried out included % immersion, moisture content, deacetylation degree, solubility of chitosan, odor, texture and color.

| Parameter                  | Chitosan obtained | International Standart |
|----------------------------|-------------------|------------------------|
| % yield                    | 58%               | 10 %                   |
| Water content              | 0.0483 %          | 10 %                   |
| Deacetylation degree       | 74.44 %           | ≥ 70 %                 |
| Solubility                 | dissolve          | dissolve               |
| Odor                       | odorless          | odorless               |
| Texture                    | powder            | powder                 |
| Colour                     | Yellowish white   | White to pale yellow   |

**Characterization with FTIR**

The results of the chitosan FTIR spectrum analysis showed absorption in the wave number area 3448.24 cm^{-1} OH stretching and NH (-NH_2) amine, absorption area of the wave number 3267.05 cm^{-1}
and 3110.14 cm\(^{-1}\) HH (\(\text{NHCOCH}_3\)) amide II, wave number area 2925.00 cm\(^{-1}\) and 2891.52 cm\(^{-1}\) (doublet) CH stretching (CH ring, CH\(_3\) and \(-\text{CH}_2\)-), absorption area 1657.13 cm\(^{-1}\) and 1625.56 cm\(^{-1}\) (doublet singlet) C = O stretching (\(\text{NHCOCH}_3\)) amide I, absorption at the area of 1417.67 cm\(^{-1}\) and 1379.01 cm\(^{-1}\) CH bending (C-Hring: \(-\text{CH}_3\); \(-\text{CH}_2\)) and CC, absorption at wave number 1157, 22 cm\(^{-1}\) bridge-O-stretching (COC) and wave number area 1074.72 cm\(^{-1}\) and 1026.37 cm\(^{-1}\) C-Oasym and C-Osym stretching. The chitosan powder obtained was 65.9 g.

Figure 2 Chitosan FTIR Spectrum

**Chitosan-CuO**

The results of FTIR spectrum analysis of chitosan-CuO (2:1) showed absorption in 3448.87 cm\(^{-1}\) OH stretching and NH (-NH\(_2\)) amine wave numbers, absorption area of 2926.22 CH stretching area, absorption area of 1655.65 cm\(^{-1}\) and 1560, 79 cm\(^{-1}\) (singlet doublet) C = O stretching (\(\text{NHCOCH}_3\)) amide I, absorption at wave number area 1156.78 cm\(^{-1}\) bridge-O-stretching (COC) and wave number area 1073.04 cm\(^{-1}\) and 1026.50 cm\(^{-1}\) C-Oasym and C-Osym stretching.

Figure 3 Chitosan-CuO FTIR Spectrum

**Adsorption of chitosan-CuO to heavy metals**

The reduction in adsorption presentation is suspected because the amine and hydroxyl groups contained in chitosan are already full binding to other components (H +) or already saturated. Under too long adsorption conditions, metal ions that have been bound by the adsorbent (chitosan) can be released again or caused by a low temperature, the bonds that occur are weak bonds. The longer the adsorption
process takes place, the more alkaline the solution will be, so that the chitosan adsorption power decreases and becomes more ineffective [15]. The longer the time of immersion with chitosan-CuO composite solution, the more the levels of heavy metal ions are bound by the amino group. However, based on the results of the study by Khairuni et al., (2017), it was shown that the 45-minute soaking time was more effective in absorbing the metal.

Chitosan-CuO, which is black in the form of granules, was inserted into the column, then added with the sample that has been decomposed, bubbles occurred and the sample water changed to light blue and a brownish precipitate was formed and filtered to produce a clear greenish blue filtrate before being analyzed with atomic absorption spectrophotometer (AAS) at 217 nm wavelength. Based on the research that has been done, the ability of chitosan-CuO composites to absorb Hg metal in white cream X obtained before being adsorbed is respectively 7.1388 ppm and after adsorption in a row 0.9253 ppm. This indicates that the Hg metal absorbed is around 87%.

4 Conclusion
This study has succeeded in synthesize chitosan from shrimp shells with the quality of chitosan produced, among others; 0.0483% water content, solubility in acetic acid can dissolve completely, 58% yield, and degree of deacetylation of 74.44%, odorless, yellowish white. Characterization of compounds in physics and chemistry identified that the compounds produced were chitosan. Chitosan-CuO composites were able to adsorb heavy metals with absorbency to mercury (Hg) at 87%.

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