

The Potential of Chitosan Polymer Waste as Bioremediation Agent of Cu(II) Ions

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Abstract:- Chitosan is a derivative of chitin by partial deacetylation process. Fishery waste is a major source of chitosan. Southeast Sulawesi is a coastal area of the fishery waste producer abundantly. The potential of high shrimp waste is major opportunity of chitosan industrial development. One of the utilization of chitosan is good enough as a bioremediation agent of Cu (II) ions. This study uses a shell shrimp (*Penaeus monodon*) as source of chitin. The transformation of chitin into chitosan by reaction with base to produce high concentrations of chitosan with degree of deacetylation of 60%. The ability of chitosan to absorb Cu (II) ion at pH 6 with various concentrations of 20-50 ppm and contact time of 30-240 min showed proportional data. The higher concentration of metal ions to make contact with the chitosan (powder and membrane), caused the number of ions that absorbed increasing. The longer contact of chitosan (powder and membrane) at all concentrations showed increasingly high number of Cu (II) which absorbed. The ability of chitosan (powder and membrane) to adsorb Cu (II) reached 50 ppm and the adsorption > 60%. These results should be considered related to the application of chitosan on the handling of environment.

1. Introduction

Urban development is always followed by the growth of industrial sector. The growth causes excess of water consumption, resulting in the release of various types of pollutants dissolved, such as toxic heavy metals, dyes, pesticides, humic substances, detergents and other persistent

pollutants. Several treatment methods such chemical precipitation, ion exchange, reverse osmosis (RO), oxidation/reduction, adsorption, filtration, coagulation, electrolysis, vaporation, electroplating, activated sludge, aerobic and anaerobic treatment, etc. have been used to remove the pollutants [16]. The release of metal ions of copper in the water can occur through

metal cleaning and plating baths activities, pulp, paper board mills, printed circuit board production, wood pulp production and fertilizer industry. The presence of copper ions in the human body have a positive impact on the lower level. According to safe drinking water act, copper has a permissible limit of 1.3 mg/L in drinking water [17]. In human beings, ailments such as stomach upset and ulcers, liver and brain damage are caused by the excess concentrations of copper [18].

Indonesia as a maritime country has natural resources that very abundant aquatic. The processing of aquatic product leaves residual waste that can not be used optimally. Fishery waste potential such as crab and shrimp shells are organic polymer compound that has reactive group (acetyl/amino) and wide application [13-15]. Chitin and chitosan have been widely reported the ability to bind the different types of metals effectively. Functional properties of chitosan in environmental applications have been reported by Mahmoodi et al [10], Mohamed and Ouki [9], Chang and Chen [8], Wang et al [7], Zhang et al [6] and Zhao et al [5] namely, the ability to absorb dye (DR80, DR81 and RR 180), ethylbenzene, Gold (III), Au (III) and Pd (II), rhodamine B, Ni (II) and Cr (VI). In this study will be reported the isolation of chitosan from shrimp shells and its application in absorption of Cu (II) ion.

2. Materials and Methods

2.1 Materials

All materials used in this work were analytical grade. Sodium hydroxide (NaOH, $\geq 99\%$), hydrogen chloride (HCl, $\geq 37\%$), *n*-hexane (C₆H₁₄, $\geq 99\%$), ethanol (C₂H₅OH, $\geq 99\%$) were purchased from Merck, Germany. Hydrogen peroxide (H₂O₂, $\geq 30\%$), Copper (II) sulphate pentahydrate (CuSO₄.5H₂O, $> 98\%$), acetic acid (CH₃COOH, 99,7%) and Sodium diethyldithiocarbamate trihydrate

(C₅H₁₀NaNS₂.3H₂O) ($\geq 99,7\%$) were purchased from Sigma-Aldrich, Singapore.

2.2 Methods

2.2.1 Extraction of chitosan

The chitin source was obtained from shrimp shell waste from one of fishery company in Kendari in Southeast Sulawesi, Indonesia. The extraction of chitin through deproteinization step using NaOH 5 M (1:10 at 60°C for 2h) [4] and demineralization using HCl 1.25 M (over night and room temperature) [3]. The next step is the reaction of deacetylation of chitin using NaOH 50% (1:10, at 90°C for 4h). That process is the final step isolation of chitosan. All phases were conducted washing using water before going on the next step. To eliminate the pigment carotene on chitin and chitosan was performed decolorization using H₂O₂.

2.3 Characterization of chitosan

2.3.1 Determination of the degree of deacetylation

Determination of the degree of deacetylation of chitosan was conducted using infrared spectroscopy. Samples were prepared by 1% KBr pellet then performed scanning at frequency range between 4000-400 cm⁻¹. Degree of deacetylation was carried out with "base line" method [2].

2.3.2 Water content, ash content and solubility

Determination of water and ash contents of chitosan were carried out using the standard method of AOAC (1984). Whereas, the solubility of chitosan was carried out according with Rinaudo [2] method.

2.3.3 Determination of molecular weight

Determination of molecular weight of chitosan is determined according to the equation of Mark-Houwink-Sakurada [2].

2.4 Preparation of chitosan membrane

1 g of chitosan was dissolved in 1 M acetic acid and stirred using a magnetic stirrer for 24 hours. The gel formed was made a sheet and

dried at room temperature. Chitosan membranes formed were washed with 0.1 M NaOH solution and distilled water and then dried again at room temperature [20].

2.5 Application of chitosan (Powder and membrane)

The ability of chitosan (powder and membrane) absorb Cu^{2+} ion was carried out by physical contact in a solution containing 20-50 ppm Cu^{2+} . Contact time was varied for 30-240 min. All solutions are Cu^{2+} at pH 6.

3. Result and Discussion

3.1 Extraction of chitosan

Chitosan is a chitin derivative products through partial deacetylation process using high concentrations of base. Chitin and Chitosan are linear polymer composed of poly (β - (1 \rightarrow 4) -N-acetyl-D-glucosamine) and poly (β - (1 \rightarrow 4) -D-glucosamine). Extraction of chitosan begins with deproteinization process using a strong base of low concentration. Deproteinization mechanism is through breaking of chemical bonds between the polymer chitin and protein. NaOH reaction with protein unit will produce sodium protein as salt. Protein component contained in shells or shrimp can act as an agent allergic to most humans, so deproteinization is necessary. A wide range of chemicals have been tested as deproteinization reagents including NaOH, Na_2CO_3 , NaHCO_3 , KOH, K_2CO_3 , $\text{Ca}(\text{OH})_2$, Na_2SO_3 , NaHSO_3 , CaHSO_3 , Na_3PO_4 and Na_2S [4].

The second step of chitosan extraction is the removal of a strong mineral acid which is called demineralization. Demineralization is the process of removing minerals, especially calcium carbonate. Generally demineralization is performed by acid treatment using HCl, HNO_3 , H_2SO_4 , CH_3COOH and HCOOH [1]. Demineralization process was performed using a 1.25 M HCl solution (1:10 w/v) as the most

effective reagent. Demineralization continued for 24h (Room temperature). The use of high concentrations of acid should be avoided as it causes depolymerization of the polymer chain. Results obtained in deproteinization and demineralization steps are product neutral and dried (70-80°C). With the passing step of deproteinization and demineralization, the extract obtained can be called chitin. The transformation of chitin into chitosan was conducted through partial deacetylation of chitin reaction (-OCH₃) using 50% NaOH. In addition base, acid groups can also be used for the deacetylation of chitin, but the glycosidic bond is very susceptible to acid polymer. Therefore, the use of base is recommended [12]. Degree of deacetylation (DD) of chitosan obtained in this study reached 60% under the reaction conditions of 90°C for 4h. DD calculation using base-line method based on the FTIR spectrum (Figure 1).

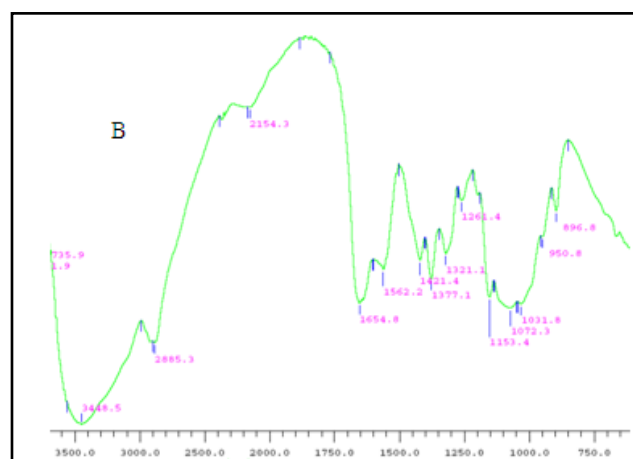
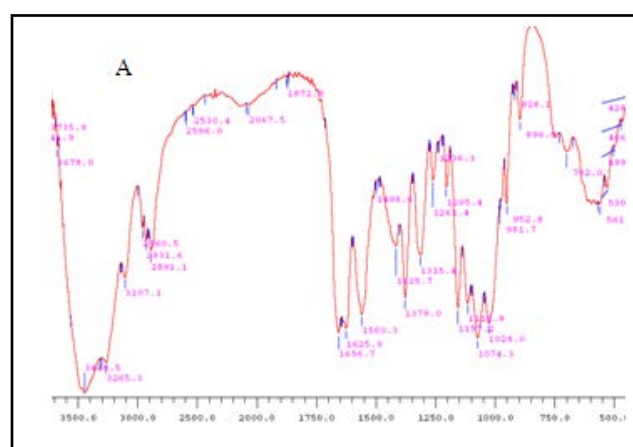


Fig. 1. FTIR spectra of (A) Chitin and B)

The chitosan polymers. The obtained absorption peak around 3448 cm^{-1} indicating the -OH stretching vibration, absorption peaks at 3103 cm^{-1} showed asymmetric stretching vibration NH (NHCOCH_3 , Amide II), absorption peaks at 2931.6 and 2885.3 cm^{-1} showed absorption CH_3 and CH stretching of aliphatic alkanes [22]. The other absorption peaks appeared on the 1656 cm^{-1} band showing the stretching group C=O (NHCOCH_3 , Amide I); peak at 1311.5 cm^{-1} band showing the C-N stretching vibration. The spectra of chitosan (Fig. 1B) showed the change in absorption around 3400 cm^{-1} becomes wider and shifted toward the wave number is smaller, the intensity of the absorption peak around 3200 cm^{-1} indicates that the group N-H (Amide II) is getting low and lost. This is most likely due to overlapping with absorption NH_2 and OH. Another indication of the release of acetyl groups on chitin are getting low intensity of absorption at 1650 cm^{-1} band showing the stretching vibration of C=O groups and the increasing absorption at 1550 cm^{-1} band showing the N-H bending vibration of $-\text{NH}_2$. Determination of the degree of deacetylation through spectra performed using the baseline that has been reported by Khan [11], comparing the absorbance at amide groups and hydroxyl groups. In this research, the DD of chitosan is 60%. Chitosan results of this study have water and ash contents of 8% and 1%. Perfect solubility has been shown in a solution of dilute acetic. The molecular weight of the resulting chitosan is $7.2 \cdot 10^5$. The different results have been reported by No. and Meyer [21] which resulted in the molecular weight of $0.12\text{-}1.5 \cdot 10^6$. Small WM an indication depolymerization.

3.2 Application of chitosan

Application of chitosan in this study is adsorption test of chitosan on Cu (II). This

reaction takes place at acidic pH conditions. Adsorption properties of chitosan be studied on the contact time of 30-240 min. While, the concentration of Cu (II) was varied from 20-50 ppm. The results showed that the different effectiveness of the chitosan powder and membrane adsorptions shown in Figure 2. The longer of contact time of chitosan powder/membrane shows the number of Cu (II) adsorbed higher. The contact of chitosan and metal ion that too long, can decrease or release metal ion that has been bound to the active site

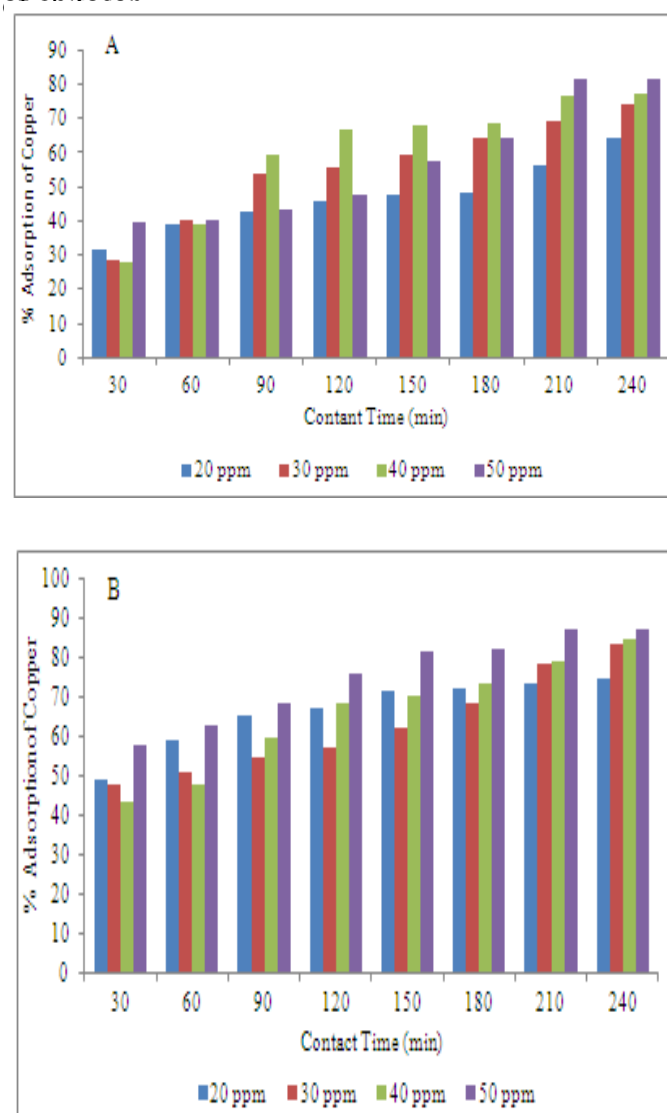


Fig. 2. Effect of contact time on Cu (II) adsorption by chitosan (A: Powder, B: Membrane).

The ability of chitosan to absorb metal ions optimally. In this study showed that the model membrane is more effective than powder, because the ability of the membrane can occur swelling on contact with liquids. Increasing of membrane volume causes mobility of polymer chain increased so as to facilitate the penetration of solvent. This interaction will produce a chemical bond that stronger than the interaction on powder that are greatly affected by agitation. NH_2 group in the chitosan acts as provider of electron pairs for metal ions to form stable complexes through coordination bonds [4].

4. Conclusion

Chitosan that extracted from shrimp shells was applied as an adsorbent Cu (II) ion. The variables that considered in this application are the contact time and the concentration of adsorbate. Application of chitosan powder and membrane has a different absorption. Either membrane and powder showed that if the contact time and the concentration Cu (II) ion increase, the number of ions absorbed higher.

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