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Development of Bioadsorbent Chitosan from Shrimp Shell Waste to Mercury Absorption Efficiency

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Abstract. This study aims to develop chitosan bioadsorben from shrimp shell waste that is applied to water samples in unlicensed mining activities in the Bone River of Gorontalo Province. The properties of chitosan were characterized, such as the determination of water content, ash content, solubility test and determination of acetylation degree by using FTIR. Prior to the application of chitosan products into samples in unlicensed mines locations, a qualitative metal mercury test was conducted on the samples using specific reagents for mercury metals, namely HCl, KI, NaOH, and NH3. The result showed that chitosan deacetylation degree was 73.88%, characterization test fulfilled chitosan standard requirement that was ash content 0.4%, water content 6.48% and soluble in acetic acid. Chitosan products from shrimp shell waste can be used as an environmentally friendly bioadsorbent that can reduce the level of mercury metal in the unlicensed mining activities in the Bone River of Gorontalo Province by 54.90%.

1. Introduction

Heavy metal pollution is one of the most serious threats to aquatic ecosystems because it is potentially toxic, even at very low concentrations. Heavy metals do not decompose on living organisms and tend to accumulate [1][2]. Mercury (Hg) is one of global pollutant which may give bad impacts to human health and ecosystem [3].

Several techniques have been applied to remove this heavy metal such as ion exchange, solvent extraction, ultrafiltration, adsorption, and coagulation [4][5]. However, the application of some of these methods may be impractical due to economic constraints or may be insufficient to meet strict regulatory requirements. Furthermore, they may generate hazardous products or products which are difficult to treat [6]. Adsorption had been reported as an efficient method for the removal of heavy metals from aqueous solution because of their effectiveness even at low concentration [2][7].

According to Lertsutthiwong [8], chitosan could be obtained from chitin via deacetylation process. It has a free amino group which might be able to bind metal ions. It has been employed to remove heavy metal ion from the effluent. Chitosan and its derivatives are cheap and effective as a heavy metal adsorbent [9]. Both chitin and chitosan are not toxic and biodegradable [10][11].

Chitosan and its derivatives displayed good adsorption capacities toward arsenic [12]. Adsorption of mercury heavy metals in chitosan occurs by coordination with amino groups or in combination with vicinal hydroxyl groups, an electrostatic attraction in acidic media or ion exchange with protonated amino groups [13].

Shrimp is abundant natural resources particularly, in Gorontalo Province. In several traditional markets in Gorontalo, it was observed that the shrimp shells were discarded and was left to rod without any further treatment and may lead to environmental pollution and damage environmental aesthetic. These problems might be solved by applying the shrimp waste as the source of chitosan. Several reports showed that chitosan displayed good activities in the adsorption of Hg(II) [14] and Pb(II) [15] ions. Lukum reported that chitosan obtained from Gorontalo shrimp shells wastes has deacetylation degree of 80% and was able to adsorb Pb(II) from sugar factory Tolanghua, Gorontalo [16][17].

The adsorption capacity of metal ions in chitosan depends on crystallinity, affinity for water, deacetylation rate and amino group content [18]. The design of a chitosan filter for the removal of metallic ions from contaminated effluents requires equilibrium and kinetics data for the system [19]. Kinetics studies show that the rate of adsorption of metal ions to chitosan depends on raw materials, preparation methods, chemical modification, and the size and shape of chitosan particles [18]. Numerous studies have demonstrated that chitosan posses a great sorption capacity and favorable kinetics for most metals. Reviews have been presented by Wu et al. [20] Reddad et al. [21] and by Gerente et al. [22].

2. Method

The shrimp shells were obtained from Gorontalo. Shrimp shells were washed and dried on the open air. It was then ground by using a mortar and sieved to give 90 mesh size. Isolation of chitosan [8] was carried out with the following steps: deproteination, demineralization, depigmentation, and deacetylation.

The properties of chitosan were characterized, such as the determination of water content, ash content, solubility test and determination of acetylation degree by using FTIR [23]. The degree of acetylation was determined using the baseline method by Sabnis and Block from FTIR using the following equation [24].

$$\% DD = 100 - \left[\left(\frac{A_{1655}}{A_{3450}}\right) \times 115\right] \quad (1)$$

where, A (Absorbance)= $\log(P_0/P)$, A_{1655}= Absorbance at wavenumber 1655 cm^{-1} for the absorption of amide/acetamide (CH_3CONH), and A_{3450}= Absorbance at wavenumber 3450 cm^{-1} for the absorption of hydroxyl (-OH) group.

The content of water in chitosan affects the storage period of chitosan. Water content is an important parameter and requires no more than 10%. Determination of ash content is done to know mineral contents that have not lost at demineralization stage. Separation of mineral content is done using HCl solution. The solubility test was used water, HCl, HNO_3, NH_3, Na_2SO_4, and CH_3COOH 1%.

Mass and pH for the mercury metal adsorption process in unlicensed mining waters in the Bone River, used from previous optimization results reported by Lukum [23]. Optimum chitosan mass equal to 1.2 gram and optimum pH 8, with an adsorption time of approximately 30 minutes.

Prior to the application of chitosan products into samples in unlicensed mines locations, a qualitative metal mercury test was conducted on the samples using specific reagents for mercury metals, namely HCl, KI, NaOH, and NH_3. The water samples were taken from 5 different locations in the village around the river Bone. The qualitative test was performed by preparing 4 tubes of reaction and filled each with 5 mL of wastewater sample. To the tube were added each of the specific reagents HCl 0.5 M, KI 0.5 M, 0.1 M NaOH and NH_3 0.1 M dropwise.

Determination of Hg(II) concentration: Solution of Hg(II) ion was carried out using Atomic Absorption Spectroscopy (AAS) based on SNI 01.1754:-6-2006. The obtained absorbance was introduced to the equation y = a + bx to obtain the concentration of Hg(II).

3. Result and Discussion

Chitosan is a derivative product of chitin polymer that is a by-product (waste) from the processing of fishery industry, especially shrimp and crab. Shrimp shell material comes from Gorontalo Province, Indonesia. Chitosan had been isolated from the shrimp (*Penaeus monodon*) shells through deproteination, demineralization, depigmentation and deacetylation process. The isolation stage is performed to produce chitosan from shrimp shells that are free from impurities. Shrimp shells were washed and dried on the open air.

The chitosan isolation process has been reported by Lukum [23], which is then used for the adsorption of Hg (II) ions for samples at unlicensed mines locations. Lukum [23] reports that the process of deproteination to remove proteins by breaking the bonds between chitin and protein in shrimp shells yielding brown powder at 51.72% results, indicating that the amount of protein attached to sodium ions is 48.28%. The product in the demineralization process is dark brown 24.98%, indicating that the amount of mineral salt is 75.02%. The process of depigmentation is done to remove carotenoid dyes to produce chitin. Chitin obtained after the depigmentation process is a light brown solid with a yield of 22.71%. Chitin obtained was a light brown solid with a yield of 22.71% and deacetylation process gave chitosan as a brownish white solid with a deacetylation degree of 73.88%, which met commercial chitosan quality standards.

The FTIR analysis result was depicted in Figure 1. The chemical analysis data of chitosan were presented in Table 1 [23].

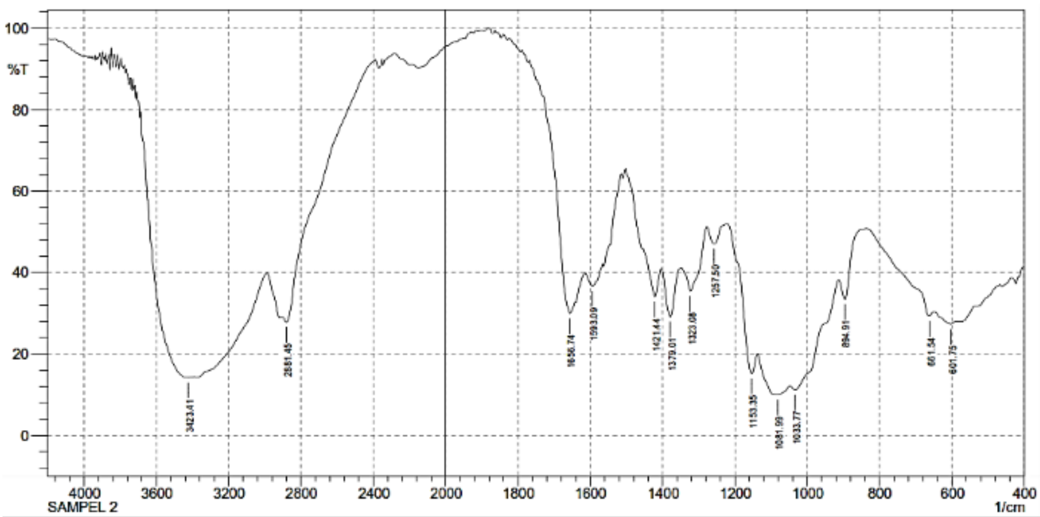

Figure 1. FTIR spectrum of isolated chitosan

One of the properties of chitosan is easily broken down by microbes/degradation. Chitosan water content depends on the relative humidity of the air around the storage area because chitosan is hygroscopic, easily absorb water from the air around 230 - 440%, especially during the storage period. The higher the water content the greater the speed of damage to a product. A good packing and storage method will produce chitosan with low moisture content. According to Sudarmadji et al. [25] a material that has undergone a drying turns out to be more hygroscopic than its original material. The high water content is also caused by the high concentration of HCl used in the demineralization process of shrimp skin. Mineral content, although low, resulted in the binding energy of chitosan to water. The water content of chitosan results of this study showed as 6.48%. This result is in accordance with the standard that is <10%.

Table 1. Chemical analysis data of chitosan isolated from the waste of shrimp (*Penaeus monodon*)

Parameter	Standard chitosan[14]	Chitosan (experimental)[16]
Water content	≤ 10 %	6,48 %
Ash content	≤ 3 %	0,40 %
Deacetylation degree	≥ 60 %	73,88 %
Solubility:		
Water	Not soluble	Not soluble
Concentrated HCl	Slightly soluble	Slightly soluble
HNO_3	Slightly soluble	Slightly soluble
CH_3COOH 1%	Soluble	Soluble
Concentrated NH_3	Not soluble	Not soluble
Na_2SO_4 2%	Not soluble	Not soluble

Ash content is a measure of the success of the demineralization process in the making of chitosan. The lower the ash content, the higher the chitosan level. The ash content analysis result is 0.40%, which is in accordance with the required ash content, ie not greater than 2%. Determination of ash content caused by the demineralization process is the process of removing minerals from shrimp waste is perfect. The chemical reaction between hydrochloric acid with $CaCO_3$ and $Ca_3(PO_4)_2$ in this process will produce calcium chloride deposited and is easily separated from the product through a wash process using a flowing acquisition allowing wasted minerals to settle and dissolve in solution.

Chitosan is not soluble in water, slightly soluble in HCl, HNO_3, H_3PO_4 and insoluble in H_2SO_4. Chitosan can only dissolve in dilute acids, such as acetic acid, citric acid, except substituted chitosan water-soluble. The presence of carboxyl groups in acetic acid will facilitate the dissolution of chitosan due to the interaction of hydrogen between carboxyl groups with amine groups of chitosan [16]. Seen from the structure, although many hydroxyl group content can form hydrogen bonds with water, the chitosan produced by the sting is difficult to dissolve. In cellulose, too, although it contains hydroxyl groups that can form hydrogen bonds with water, cellulose is very difficult to dissolve. This is due to chain stiffness and high inter-chain forces due to hydrogen bonds between hydroxyl groups in the interconnected chains.

The chitosan produced in this study had the same solubility properties as standard chitosan, ie dissolved in dilute acetate, slightly soluble in HCl, HNO_3, and water-insoluble, NH_3, and $NaSO_4$. Acetic acid is classified as a weak acid carboxylic acid group-containing carboxyl group (-COOH). The carboxyl group contains a carbonyl group and a hydroxyl group. The boiling point reached 118 ºC and very sharp smell [26].

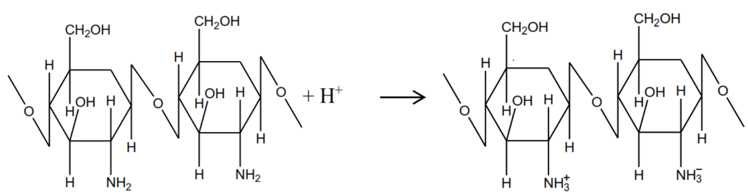

Figure 2. Reaction of chitosan dissolution in 1% acetic acid solution

A pair of free electrons in a hydrogen atom causes the amino group on the chitosan to be Lewis base. When chitosan is dissolved in acetate, the amino group will bind H^+ ions and form a chitosan compound which is cationic [16].

Qualitative tests were conducted on water samples in the waters of the Bone Gorontalo river, Indonesia, in areas in unlicensed mines locations.

Table 2. Qualitative data of mercury metals in Bone river water samples

Reagents	Reaction	Observation result	Conclusion
HCl	$Hg^{2+} + 2Cl^- \rightarrow HgCl_2\downarrow$	White deposits	Positive Hg
NaOH	$Hg^{2+}+2OH \rightarrow Hg(OH)_2\downarrow$	White deposits	Positive Hg
KI	$Hg^{2+} + 2KI^- \rightarrow HgI_2\downarrow$	Sludge of red brick	Positive Hg
NH_3	$Hg^{2+}+NH_3 \rightarrow Hg(NH_3)_2\downarrow$	Yellow deposits	Positive Hg

Based on the Table, it is seen that the five specific reagents used showed positive samples containing mercury metals. Furthermore, to determine the mercury metals levels in this study used analysis using AAS.

Quantitative test of water samples using AAS is done before the adsorption process using chitosan. The results of the analysis indicate that all unlicensed mines locations are contaminated by mercury metals.

Table 3. Quantitative test of mercury metals at unlicensed mines locations using AAS analysis

Location	Concentration (μg/L)
Mohutango Village	2,04
Poduoma Village	0,22
Pangi Village	0,09
Bulabo Village	0,07
Tilangobula Village	0,01

This is left unchecked would result in the environment of the five villages becoming insecure for the good lives of people and animals in the area. Therefore, there should be an effort to overcome these environmental problems by way of utilizing the product of chitosan technology which is the base of shrimp shell waste that can be used as bioadsorben environmentally friendly. Table 3 presents the results of prospective chitosan adsorbent utilization on mercury metals in water samples from the five unlicensed mine locations, Bone River, Gorontalo.

Chitosan products from shrimp shell waste produced to absorb mercury metals by 54.90% in the first location in Mohutango Village which is upstream of the river where unlicensed mining activities. The ability of chitosan adsorbs metal is due to the presence of amino and hydroxyl groups. Based on a series of ligand strengths in the spectrochemical, the hydroxyl group is located to the left of the amine group, so that the amine group is stronger than the hydroxyl group in adsorption. This means that in the process of adsorption the metal ions are more readily bonded with the amine group than to the hydroxyl group [27][28].

Table 4. The mercury metal test results after adsorption using the Batch Method

Location	Hg concentration after adsorption (μg/L)	Removal Hg (%)
Mohutango Village	1.12	54.90
Poduoma Village	0	100
Pangi Village	0	100
Bulabo Village	0	100
Tilangobula Village	0	100

Chitosan interactions with metal ions occur because of complexing processes, ion exchange processes, and chelating that occur during the process. The three processes depend on the metal ions. Chitosan shows a high affinity in the class 3 transition metals and on non-alkali metals with low concentrations [29].

The chitosan active sites in either NH_2 form or in NH_3^+ protonated state are capable of adsorbing heavy metals through chelating and/or ion exchange mechanisms. The presence of such groups causes chitosan to have high reactivity and may act as a substituted amino because of its cation polyelectrolyte properties [30]. The deacetylated amino groups cause chitosan to have the greater capability as a complexing ligand (chelate) of transition metal ions such as Mn, Co, Ni, Cd, Zn, Cu, and Hg compared to chitin [31][32]. The free electron pair of N atoms in the amino group will then bind to the metal ion, as in the following reaction:

$$R\text{-}NH_2 + H^+ \rightleftharpoons R\text{-}NH_3^+ \qquad (2)$$

Reaction (1) shows the protonation and deprotonation of amino groups in chitosan. When chitosan is added in a metal ion solution it is likely that the reaction will occur as follows:

$$R\text{- }NH_2 + M^{2+} \longrightarrow R\text{-}NH_2M^{2+} \qquad (3)$$

$$R\text{- }NH^{3+} + M^{2+} \longrightarrow R\text{-}NH_2M^{2+} + H^+ \qquad (4)$$

R is a component other than the -NH2 group in chitosan and M is the Hg metal.

When reaction 2 takes place, the free electrons of the N atom interact with metal ions. Reaction (4) has the same mechanism as reaction (3), although the chitosan-NH_2 group has changed to positively charged by receiving H^+ ions from the environment. The interaction between metal ions and N atoms of reaction (3) is stronger than the bond between H^+ ions and N atoms of reaction (4) (protonation of amino groups). This is due to the strength of the electrostatic interaction between the free electron pairs of N atoms with polyvalent metal ions stronger than the electrostatic interactions between the free electron pairs of N atoms with monovalent protons (H^+) [28].

Adsorption of chitosan against metal ions at low concentrations is likely forming a chelate bond between metal ions and amino groups. While at high concentrations the urgency of metal ions to chitosan is very large, consequently not only binding amine groups, but simultaneously hydroxyl groups also play a role, so that no longer formed monolayer but tends to multilayer [33].

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4. Conclusions

Chitosan products from shrimp shell waste can be used as an environmentally friendly bioadsorbent that can reduce the level of mercury metal in the unlicensed mining activities in the Bone River of Gorontalo Province by 54.90%.

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