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Time Stirring Effect of Chitosan from Shrimp Shells as Gold Absorbent

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Abstract
This study aims to analyze the effect of chitosan stirring time from shrimp shells as gold absorber. Experimental research was conducted in this study, where the manufacture of chitosan from shrimp shells began with demineralization (mineral removal) using 1.5 M HCl, deproteination (protein removal) using 3.5% NaOH and deacetylation (acetyl removal) using 60% HCl. The chitosan formed was weighed 0.1 gram (as many as five samples) and then stirred in a 10 ppm Au solution, with a stirring time of 0, 10, 20, 30, and 40 minutes, and its absorption ability to gold was analyzed using AAS (Atomic Absorbsion Spectroscopy) and obtained percentage of absorption respectively 24.79%, 50.89%, 45.64%, 40.52% and 37.87%. From the results of the study, it was found that there was an effect of chitosan stirring time from shrimp shells as gold absorber and the highest absorption at 10 minute stirring was 50.89%.

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INTRODUCTION

Indonesia is rich in natural resources in the fields of agriculture, plantation, mining and fisheries. Indonesia's geographical location also causes the size of the sea area so that the potential in the fishery sector is so great. In the Province of West Nusa Tenggara (NTB) especially in Lombok one of the abundant fisheries products is shrimp. Utilization of shrimp so far is only limited to the contents for consumption while the shell or skin is thrown away so that the shrimp shells become waste and environmental pollution. Meanwhile, Indonesia is also rich in gold mining. Gold mining is spread in almost all islands in the territory of Indonesia including Lombok and Sumbawa in the NTB province. Gold mining in NTB is mainly in several locations such as in Sekotong (West Lombok), Labaong, Marente and Dodorinti (Sumbawa), and Hijrah (West Sumbawa), as well as several other places in NTB. The mines are managed by the people (community mines).

Gold is included in the group of precious metals, called precious metals because of their scarce number, their beauty with a shiny yellow color and their usefulness (Aitio et al., 2015). The processing of gold ore from mining activities carried out by the large-scale gold ore processing industry generally uses the cyanidation process, namely the extraction of gold metal by means of extraction using cyanide solvents (Hardiani, 2002). The cyanidation method is used because the process provides a relatively large recovery value, which is 90-97%. Cyanide is one of the B-3 compounds (Dangerous and Toxic Material) (Siregar, 1999). The use of cyanide as a solvent for gold metal extraction is limited to 1,500 ppm (Siregar, 1999). The cyanidated ore processing process will produce liquid waste known as tailling effluent containing cyanide, the waste is necessary and must be treated so as not to endanger the environment (Sutoto, 2007). High concentrations of cyanide can have harmful effects on the environment and living things around it, including on aquatic ecosystems, terrestrial animals and humans. Based on observations made at several gold mining sites in NTB, it shows that the gold separation process is carried out using materials that are not environmentally friendly such as cyanide and mercury which can cause damage and environmental pollution. This problem can be overcome by reducing or avoiding its use and of course looking for other alternatives as absorbent materials, one of which is by using chitosan.

Chitosan is a carbohydrate (polysaccharide) compound produced from fisheries waste, especially crustaceans namely shrimp, crabs and shellfish (Sari & Abdiani, 2015), is a semi-synthetic aminopolysaccharide that can biodegrade biologically and has various applications in the biomedical industry and others (Agarwal et al., 2013). Chitosan is a natural polymer compound from chitin derivative that has undergone a process of isolation, deprotetination, and demineralization (Agustina et al., 2015). The structure of chitosan is a non-linear chain polymer which has the general formula of the molecule $(C_2H_{11}NO_4)n$ or is referred to as poli- (2 amino-2-deoxy-β- (1-4) -D-glucopyranose) (Sugita et al., 2009).

Chitosan can adsorb several metals, based on research results that chitosan can adsorb Hg2+ ions (Rahayu, 2007), adsorb Pb2 + ions (Sanjaya, 2007), adsorb Cr3+ and Cu2+ ions (Apsari, 2010). Chitosan can be made from materials containing chitin such as crustaceans (shrimp, lobster and crabs), fungi, worms, cockroach octopus and others, while in Lombok there is a lot of shrimp shell waste. The waste can be used as raw material for making chitosan because the chitin content is quite large, namely 20-30%, so it becomes an alternative in reducing shrimp shell waste. In making chitosan is influenced by several factors, namely the source of chitin, temperature, concentration of solution, and duration of stirring, in this study only looked at the effect of stirring time. Making chitosan from shrimp shell waste is expected to increase the economic value of shrimp shells and make chitosan as an environmentally friendly gold absorber.

METHODE

This study is an experimental research conducted in a laboratory to analyze the effect of chitosan stirring time from shrimp shells as gold absorber. The tools used in this study are a set of grinding tools, magnetic stirrer with heater 79-1, memmert oven UNB-400, ohaues analytical scales, stopwatch, AAS spectrophotometer, Stative and clamps, universal pH, thermometer, magnetic stirrer, centrifugation tools , funnels, 80 mesh sieves, volume pipettes, measuring flasks, beaker cups and other chemical tools commonly used in the laboratory. The materials used in this study were shrimp shells collected from the Ampenan Kebon Roek Market, HCl pa, NaOH pa, CH2COOH pa, AuCl4, as standard solutions, Ninhidrine as oxidizing amine groups on chitosan, AgNO2 to identify CT ions, PP Indicators to identify OH contents, Aquades and filter paper.

Chitosan is made in several stages including: mineral removal (demineralization), protein removal (deproteination), protein removal (deproteination). Chitosan which has been prepared is characterized by several stages including: organoleptic test (odor, textured and chitosan color test), yield, moisture content, solubility of kitsan and test with ninhydrin solution.

Analysis of the chitosan adsorption capacity of Au metal was carried out by adding 0.1 gram of chitosan to 25 ml of a single solution of 10 ppm Au metal ion. The solution is then stirred using a stirrer at a speed of 50 rpm at room temperature. Stirring is stopped at 0 minutes (not stirring only soaked for 10 minutes), 10, 10, 20, 30 and 40. The solution is then filtered and the remaining concentration of Au metal is measured using the AAS Spectrophotometer and the percentage of absorption is determined by the formula:

$$\% \text{ Absorbent} = \frac{\textbf{remaining mass}}{\text{initial mass}} x\ 100\%.$$

RESULTS AND DISCUSSION

The formation of chitosan starts with the process of demineralization. The demineralization process uses 1.5 M HCl solution in a ratio of 1:15 (w/v) of powder and solvent. This demineralization process aims to remove the salts and inorganic minerals found in the shell. Salts contained in the shell such as: calcium, magnesium, phosphorus, iron, manganese, potassium, temabga, sodium, zinc and phosphorus (Agustina, et al. 2013). The process that occurs in the demineralization process is that minerals will react with HCl marked by the formation of CO2 gas when added to HCl so that there is a separation between the shell and the minerals contained therein. HCl addition to the sample must be done slowly and gradually so that the sample does not overflow.

Shell powder obtained from the results of demineralization then proceeded with the removal of deproteinated proteins. Deproteination process using 3.5% NaOH with a ratio of 1:10 w / v. Deproteination aims to separate the protein in the shell. The results obtained after the completion of this process are called Chitin. Chitin obtained was distilled.

Distillation was carried out using 60% NaOH, with a ratio of 1:20 w/v mass and solvent. This process aims to remove the acetyl group in chitin. The results obtained after this process are called Chitosan. The percentage of chitosan obtained depends on the percentage of yield. The percentage of chitosan yield is 9.1%, which can be seen in Table 1.

Table 1. Chitosan yield

Variable	Value
Weight of initial shrimp shell (g)	120
Weight of sample after demineralization (g)	57
Sample weight after deproteination (g)	24
Chitin yield kitin (%)	20
Weight of sample after deacetylation / Chitosan (g)	11
Chitosan yield %	9,4

The chitosan obtained was characterized to determine the quality of the chitosan produced. Characterization included water content test, solubility in acetic acid 2%, texture, color, odor, and ninhydrin test. The results of chitosan characterization obtained from the study were compared with the quality of the chitosan international standard which can be seen in Table 2.

Table 2. Chitosan characterization

Parameter	The value of chitosan obtained	Chitosan International Standard Values
Water content	-	≤ 10 %
Solubility in acetic acid 2%	Soluble	Soluble
Texture	Serbuk	Serbuk
Coluor	White	White to Pale Yellow
Smell	Does not smell	Does not smell
Test with Ninhydrin Solution	Purple	-

Chitosan obtained in this study as in Table 2, has met the value of international standards so that it can be used for various applications. The chitosan obtained had a water content of 1.55%, dissolved in 2% acetic acid, was in the form of powder, odorless, and purple when reacted with Ninhydrin solution.

The measurement of Au metal concentration before and after the adsorption was determined by Atomic Absorption Spectroscopy (AAS). Determination of Au content that is absorbed before and after absorption is determined by AAS. The results of measurement of Au metal content before and after absorption can be seen in Table 3 and Figure 1.

Table 3. Percentage of Au absorbed

Initial Au concentration (ppm)	Stirring Time (minutes)	Absorbed Au concentration (ppm)	% Absorption
8,55	0	2,12	24,79
8,55	10	4,35	50,89
8,55	20	3,90	45,64
8,55	30	3,46	40,52
8,55	40	3,24	37,87

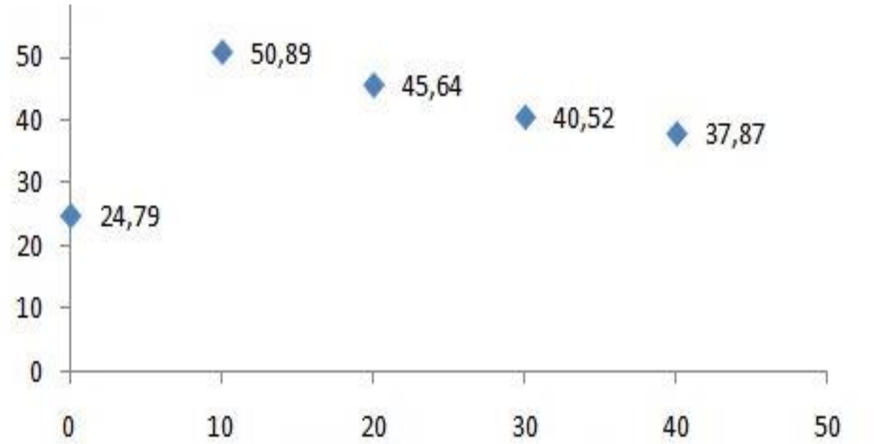

Figure 1. Graph of absorption percentage of stirring time

Chitosan absorption ability is influenced by several factors including temperature, stirring time, stirring speed, solution concentration and mass of chitosan. Stirring is one of the factors that influence the absorption ability of chitosan so it is very important to analyze. Stirring can make particle sizes relatively uniform. The longer the stirring is carried out, the smaller the size of a particle. Stirring can also make the solution mix evenly. The role of chitosan stirring In absorbing gold affects its absorption ability such as stirring carried out for 0 minutes (without stirring) only soaking chitosan for 10 minutes can absorb 24.79%, in contrast to stirring for 40 minutes chitosan can absorb gold of 37.87%, but if stirring for 30 minutes chitosan is able to absorb gold by 40.52%, while stirring for 20 minutes can absorb by 45.64%, and stirring for 10 minutes can absorb 50.89%, this proves that the absorption of chitosan to gold is better if stirring is done rather than without stirring.

The ability of chitosan to absorb gold metal (Au) based on the optimum stirring time in the 10th minute its absorption becomes 50.89%, in contrast to the absorption of chitosan to lead metal (Pb), lead metal absorption (Pb) by chitosan based on the stirring time increased over the length of the stirring time (Nurhayati, 2016), this is due to the fact that each element has different characteristics.

CONCLUSION

Based on the research results obtained, it can be concluded that there is an influence of chitosan stirring time from shrimp shells as gold absorbent and the optimum stirring time, which is 10 minutes with absorption of 50.89%.

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