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ADSORPTION FOR LEAD REMOVAL BY CHITOSAN FROM SHRIMP SHELLS

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ABSTRACT

Aim: The objective of this study is to obtain the optimum efficiency of Lead (Pb) removal by adsorption using shrimp shells chitosan. Adsorption is one of the alternative ways to treat heavy metal. Various substances can be used as adsorbents for the adsorption process. One of the natural adsorbents that can be utilized is shrimp shells. Methodology and Results: In general, the process of making chitin into chitosan includes demineralization with dilute HCl, deproteinization with dilute NaOH, then deacetylation of chitin using concentrated NaOH. This study would demonstrate the adsorption on artificial waste containing 100 mg/L of Pb using 1 gram of chitosan with variations in pH (4, 5, 6) and time (30, 60, 90 minutes) to determine the effectiveness of chitosan made of shrimp shells in reducing Pb concentration. The results show that the highest removal efficiency of lead was achieved at pH 4 and 90 minutes duration with a removal percentage of 99.88%. Conclusion, significance, and impact study: Chitosan compounds as the results of shrimp shells processing have amine groups (NH₂) which are nucleophiles (rich in electrons). It is favorable to be used as biocoagulants or bioadsorbents of lead heavy metal with a removal efficiency of above 90%.

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- Biocoagulant
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- Lead

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1. INTRODUCTION

Several alternative ways of processing metal content have been carried out; one of them is adsorption. Adsorption is the process by which fluid molecules touch and attach to the surface of solids. Various substances can be used as adsorbents for the adsorption process. One of the natural adsorbents that can be utilized is shrimp shells.

Shrimp is an invertebrate animal that belongs to the class of anthropods. The exoskeleton of animal gastropods, crustaceans, and anthropods contains chitin compounds which can be converted into chitosan compounds. Chitosan is chitin compounds that have lost their acetyl groups. The content of shrimp shells, in general, can be divided into several components such as proteins of 34.7%, CaCO$_3$ of 27.9%, chitin of 18.1%, and other constituents such as dissolved fat and digestible proteins of as much as 19.4% (Suhardi, 1992). Chitosan compounds have amine groups (NH$_2$) which are nucleophiles (rich in electrons) so that they can be used as biocoagulants or bioadsorbents. As an adsorbent, chitosan is able to absorb metal ions such as cadmium, mercury, copper chrome, and nickel. In the experiments conducted by Rahayu (2007), the adsorption using chitosan waste crab shells at pH 2, 3, 4, 5, 6 showed that the higher is pH, the higher the absorbed Mercury concentration. Another research conducted by Tiara (2014) using chitosan for metal adsorption of Pb from mining wastewater in Bangka Belitung stated that the optimum adsorption process was conducted at pH 3 with an adsorption percentage of 80.22%. Other studies found that chitosan could absorb Pb of 10.32 mg/L using 50 mg/L of adsorbent concentration and Cd of 24.9 mg/L using 100 mg/L of adsorbent concentration for 24 hours of contact time (Hendri, 2008). Therefore, this research was conducted to investigate the optimum efficiency of Pb removal by adsorption using shrimp shells chitosan in pH 4, 5, 6 and contact time of 30, 60, and 90 minutes.

2. RESEARCH METHODOLOGY

The first stage in this study is produce of chitosan from shrimp shells. The process to convert shrimp shells into chitosan was carried out through 3 stages, i.e. deproteinization, demineralization, and deacetylation. After obtaining chitosan, deacetylation degree analysis was performed to see how much shrimp shells had successfully turned into chitosan. The more chitosan formed, the greater the ability to reduce lead concentration. Before going through three main stages mentioned above, the shrimp shells were prepared in advance, including the process...
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The production of chitosan began with the preparation stage of shrimp shells. First, the shrimp shells were boiled using water at 100°C for 15 minutes, then they were dried using an oven. Subsequently, they were sieved to acquire 50 mesh shrimp shells powder. The next step is deproteinization—a process of removing the protein content found in shrimp shells by using 3.5% NaOH solution for 120 minutes at 65°C to obtain a protein-free shrimp shell.

The following stage is demineralization—a process of removing mineral content in shrimp shells by using 1N HCl solution for 30 minutes at a room temperature so that the shrimp shells are protein-free and mineral-free. The next step is deacetylation—a process to convert chitin compounds in shrimp into chitosan compounds using 50% NaOH solution for 60 minutes at 100°C.

After shrimp shells had turned into chitosan, the degree of deacetylation was determined. In this experiment, conventional methods were applied using acid-base titration with a standard NaOH 0.1N solution and the chitosan was dissolved in 0.1N HCl solution (Domard and Rinaudo, 1983). The titration was conducted by using the Methyl Red (MM)/Sindur Methyl (SM) indicator to signify the colour change from red to yellow. The degree of deacetylation shows how much chitin has turned into chitosan. The greater the percentage of deacetylation degree, the better the quality of chitosan made.

\[
\text{% degree of deacetylation} = \frac{(C_1 \times V_1) - (C_2 \times V_2)}{M \times 0.0994} \times 0.016 \times 100\%
\]

where:

- C1 : Concentration of HCl in Molar (M)
- C2 : Concentration of NaOH in Molar (M)
- V1 : Volume of HCl in milliliter (mL)
- V2 : Volume of NaOH in milliliter (mL)
- M : Weight of chitosan in gram (gr)

The next step is the analysis of lead adsorption on the simulation solution to examine the most optimum pH and contact time for the adsorption process. In this experiment, pH of 4, 5, 6 and contact time of 30, 60, 90 minutes were set. The simulation concentration of Pb were 77.66 mg/L; 77.07 mg/L; 73.09 mg/L. The Pb concentration was analyzed using ICP-OES to compare the
amount of lead concentration before and after the experiment.

### Figure 1 Flow research diagram

#### 3. RESULTS AND DISCUSSION

As explained beforehand, the degree of deacetylation shows how much chitin has turned into chitosan. The greater the percentage of deacetylation degree, the better the quality of chitosan made. During the determination of deacetylation degree using conventional methods in this study, the titration was carried out twice as a means to ensure the results, then the average volume of obtained NaOH was measured. The titration results can be seen in Table 1.

#### Table 1 Titration results

| No. | Chitosan weight (gr) | V HCl | V NaOH (mL) |
|-----|----------------------|-------|-------------|
| 1   | 0.3                  | 30    | 15.35       |
| 2   | 0.3                  | 30    | 15.65       |

As seen in the table above, the required NaOH were 15.35 ml and 15.65 ml. The average of both was then calculated and entered into the deacetylation degree formula as follows:
% degree of deacetylation = \frac{(C_1 \times V_1)-(C_2 \times V_2)}{M \times 0.0994} \times 0.016 \times 100\%

% degree of deacetylation = \frac{(0.09475 \times 30)-(0.09718 \times 15.5)}{0.3003 \times 0.0994} \times 0.016 \times 100\%

% degree of deacetylation = 70.97\%

According to Srijanto (2003), the deacetylation degree of chitosan is generally 60% and 90%–100% for full deacetylation. The obtained value of deacetylation degree of chitosan in this study was 70.96%. It corresponds well with the degree of deacetylation in Rahayu (2007) for chitosan made from crab shells of 79.65% at 90˚C and a processing time of 120 minutes.

The chitosan adsorption test was carried out using lead concentration (mg/L) as the dependent variable, while the independent variables consisted of the solution pH as well as the contact time between chitosan and solution (minutes). With the application of these variables, it is expected to evaluate the effectiveness of chitosan in reducing lead concentration and the optimum conditions for the process of lead adsorption by chitosan. The adsorption test process was conducted using a chitosan and solution ratio of 1:100, implying that 1 gram of chitosan was used to process 100 mL of lead waste solution.

The adsorption optimization test was held using a predetermined lead solution of 77.6 mg/L. The use of predetermined solution itself aims to ensure that the interaction only involves chitosan and lead alone without the presence of other disturbing elements. Thus, the results obtained are the actual outcome of lead adsorption by chitosan. The optimization test results of lead adsorption by chitosan can be seen in Table 2.

Chitosan was contacted with the simulated solution through a constant stirring. The calculation of percentage removal as listed in the table above was done by comparing the lead concentration in the solution before and after the adsorption process. It can be seen that at all pH and contact time variations, a high percentage of lead reduction of more than 98% was obtained, signifying that chitosan could be effectively used to reduce dissolved lead levels in the solution. There is also an equal lead reduction percentage of 99.81% at each pH value (pH 4 with a contact time of 90 minutes, pH 5 at 60 minutes of contact time, and pH 6 at 90 minutes of contact time). Throughout those three pH conditions, the least contact time of 60 minutes was
required for pH 5. Thus, the optimum conditions for lead adsorption process using chitosan were determined at pH 5 and contact time of 60 minutes.

### Table 2 Initial and final concentration of Pb

| Independent Variables | Initial Pb Concentration (mg/L) | Final Pb Concentration (mg/L) | Removal (%) |
|-----------------------|---------------------------------|-------------------------------|-------------|
| **pH**                | **Contact Time (minutes)**      |                               |             |
| 4                     | 30                              | 77.66                         | 0.31        | 99.60       |
|                       | 60                              | 77.66                         | 0.17        | 99.78       |
|                       | 90                              | 77.66                         | 0.15        | 99.81       |
| 5                     | 30                              | 77.07                         | 1.25        | 98.38       |
|                       | 60                              | 77.07                         | 0.15        | 99.81       |
|                       | 90                              | 77.07                         | 0.16        | 99.79       |
| 6                     | 30                              | 73.09                         | 1.28        | 98.25       |
|                       | 60                              | 73.09                         | 0.27        | 99.63       |
|                       | 90                              | 73.09                         | 0.15        | 99.79       |

*The Figure 2 show that pH 4, the percentage of Pb removal increased along with the increment of contact time (as Pb removal efficiency of 99.6%, 99.78%, and 99.81% were obtained for the contact time of 30, 60, and 90 minutes, respectively).*
Figure 3 Contact time vs removal percentage at pH 5

It can be seen in Figure 3 that at pH 5, the percentage of Pb removal increased alongside the increment of contact time at first, then decreased slightly at 90 minutes duration. With the contact time of 30, 60, and 90 minutes at pH 5, the obtained Pb removal efficiencies were 99.38%, 99.81%, and 99.79%, respectively. The removal efficiency has exceeded 90% since 30 minutes of contact time, so it can be safely said that 30 minutes is effective enough to reduce the Pb concentration in wastewater.

Figure 4 depicts that at pH 6, the percentage of Pb removal increased along with the increment of contact time as reduction values of 98.25%, 99.63%, and 99.79% were measured for 30, 60, and 90 minutes of contact time, respectively.

Figure 5 indicates that during the experiment using 30 minutes of contact time, the percentage of Pb metal removal continually decreased from 99.60% at pH 4 to 98.38% at pH 5, then 98.25% at pH 6. It could be concluded for 30 minutes of contact time, the optimum pH value to reduce the Pb concentration in the wastewater is 4. In another study conducted by Kurniasih (2014), chitosan made from shrimp shells could adsorb Rhodamine B at pH 4 and 3 with a contact time of 120 minutes and 180 minutes.

Figure 6 depicts that for 60 minutes of contact time, the percentage of Pb metal removal increased from 99.78% at pH 4 to 99.81% at pH 5, then plummeted down to 99.63% at pH 6. It can be concluded that for 60 minutes of contact time, the optimum pH to reduce the concentration of waste containing Pb is 5—unlike the optimum pH of 4 for 30 minutes of contact
time.

Figure 7 shows that the percentage of Pb removal decreased from 99.81% at pH 4 to 99.79% at pH 5, but remained constant from pH 5 to pH 6. The graph of the percentage removal at the contact time of 90 minutes is almost the same as 30 minutes. The optimum pH where the largest removal percentage occurred was at pH 4.

Figure 4 Contact time vs removal percentage at pH 6

Figure 5 pH value vs removal percentage at a contact time of 30 minutes
Figure 6 pH value vs removal percentage at a contact time of 60 minutes

Figure 7 pH value vs removal percentage at a contact time of 90 minutes

Figure 8 denotes the regression of pH and percentage of Pb removal. The relationship between the decreased concentration of Pb in the solution with the pH of the adsorption process is shown in the following equation:

\[ y = -0.675x + 102.12 \]  \hspace{1cm} (2)
where:

\[ y = \text{percentage of Pb removal (\%)} \]
\[ x = \text{pH in adsorption process} \]

Figure 8 denotes the regression of pH and percentage of Pb removal. The relationship between the decreased concentration of Pb in the solution with the pH of the adsorption process is shown in the following equation:

\[ y = -0.675x + 102.12 \quad (3) \]

where:

\[ y = \text{percentage of Pb removal (\%)} \]
\[ x = \text{pH in adsorption process} \]

It can be concluded from the results of the regression analysis on pH that increasing the pH can reduce the percentage of Pb removal during the adsorption process. It shows that low pH or acidic condition is more preferable for Pb adsorption process. On the contrary, according to Rahayu (2007), a higher pH value means a higher percentage of the pollutant removal for mercury.
It can be seen in Figure 9 that the relationship between the removal of Pb concentration in the solution with the pH of the adsorption process is shown in the following equation:

\[ y = 0.0035x + 99.52 \]  

(4)

where:

\( y \) = percentage of Pb removal (\%)

\( x \) = contact time in adsorption (minutes)

Based on the regression analysis results of contact time and Pb removal percentage, it can be concluded that prolonging contact time will increase the percentage of Pb removal during the adsorption process.

4. CONCLUSION

Chitosan from shrimp shells is beneficial to be used as biocoagulants or bioadsorbents of lead heavy metal (Pb). The optimum adsorption in this study occurred at pH 4 and 90 minutes of contact time with a Pb removal percentage of 99.81%.
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