Development of Natural Coagulant for Turbidity Removal Created from Marine Product Solid Waste

Eko Siswoyo1∗, Dian Suryani Tanjung1, M Jauhari Hamidil Jalaly1

1Department of Environmental Engineering, Universitas Islam Indonesia, Jl. Kaliurang km 14.5 Yogyakarta 55584 Indonesia

eko_siswoyo@uii.ac.id

Abstract. The presence of scallop shells, one of the marine products, increases the problem of solid waste disposal. This material is disposed to landfill without proper use, making it necessary to develop natural coagulant made from scallop shells. This research aimed to investigate the ability of scallop shells as a natural coagulant to remove turbidity. The scallop shell was used to produce chitosan, then adopted as a natural coagulant compared to a commercial product. Water turbidity, river water, and batik wastewater were examined using different coagulant doses, solution pH, and turbidity concentration. Based on data from this study, scallop shell-based chitosan has a high ability to reduce turbidity concentration in water. To remove artificial turbidity in water (14 NTU), the optimum coagulant dose was 150 mg/L and solution pH was 6. The ability of natural coagulants to remove river water turbidity (81 NTU) and batik was 72% and 87% respectively. The performance of commercial coagulant to remove artificial turbidity, river water, and batik wastewater was similar to the natural coagulant, making this novel natural coagulant a promising coagulant for water and wastewater treatment in the near future. Furthermore, massive production of natural coagulant can also solve the problem of scallop shell solid waste generation.

1. Introduction

River water and batik wastewater are often contained by suspended solids particles that cause turbidity in the water. In water treatment, the coagulation/flocculation treatment process is used to remove turbidity. The presence of a high concentration of turbidity in water can give a negative influence on human health. The study on hospital visitors, quality of drinking water, and health problems in the United States showed that there was a correlation between turbidity of drinking water and gastrointestinal illness [1], [2].

The purification of turbid water in the drinking water treatment plant requires the use of coagulants. Several natural and synthetic coagulants are available for the treatment of water and wastewater. Between the two types of coagulants, synthetic coagulants, such as alums, are materials that are mostly used in water treatment processes, because they are easier to obtain and from an economic point of view, they are also quite profitable. However, the use of synthetic coagulants may produce non-biodegradable sludge and may harm the environment and human health, as the resulting sludge is not easily recycled. Therefore, the development of natural coagulant is necessary because it has some advantages in terms of technical, economic, environmental, social aspect, sustainability [3], and safe for human health [4]. Some natural coagulants have been developed based on Kernel of Moringa oleifera and Strychnos potatorum (Nirmali) seeds [5] Cicer arietinum seed, eggplant seed and radish seed [6], and Chitin [7].
The coagulation/flocculation process using chitosan can reduce suspended solid particles and dissolved organic matter [8]. Based on previous studies, chitosan can be used as a coagulant and has better performance in reducing turbidity than alum. The use of a lower chitosan dose than alum for removing turbidity in the water proved that chitosan is more effective and efficient compared to alum as a commercial coagulant [9]. In addition, the advantages of chitosan as a coagulant are that it is non-toxic, easily biodegradable and easily interacts with other organic substances such as protein. Thus, the chitosan obtained from natural materials is environmentally friendly and has more value than synthetic coagulants [7].

Chitosan is a derivative of chitin that is obtained by deacetylation, which is the second most abundant polysaccharide on the earth after cellulose and can be found in the exoskeleton of invertebrates and some fungi in its cell walls. Chitosan comes from organic materials and has polyelectric characteristics, in the water treatment process it is very potential to be used as a natural coagulant [10]. There are many shells from marine products that contain chitin. The highest content of chitin is found in crab shells by 50% - 60%, shrimp shells by 42% -57% and scallop shells by 14% -35% [11].

Scallop shell (Amusium pleuronectes) is often found in many places in Indonesia. However, fresh scallop shells caught by fishermen are only used as food ingredients, then some of the scallop shells waste is used for handicraft materials, and some are disposed into the environment without proper use and sometimes become solid waste that can damage the environment. Based on these problems, this paper aimed to study the use of scallop shell waste to produce chitosan as a natural coagulant for the purification of water. Sample water with artificial turbidity, Mataram river water and batik wastewater will be used in this research to find out the performance of this natural coagulant for removal of artificial and real water turbidity.

2. Materials and Method

2.1. Preparation of scallop shell-based chitosan
Scallop shell waste (Amusium pleuronectes) was obtained from Losari, Wukirharjo, Sleman, Yogyakarta. To produce chitosan, 50 g of scallop shell waste with size 100 mesh was employed. There are three stages in producing chitosan from scallop shell waste. In the first stage, deproteination, 50 g of powdery scallop shell waste was put into 3% of NaOH solution (1:6) and heated at 85 °C for 30 minutes. The mixture was cooled and filtered, then the residue was washed with aquadest until the pH became neutral and dried in the oven at 80 °C for 5 hours. The second stage is demineralization, the residue resulting from the first step was poured into 1.25 N HCl solution (1:10) and heated at 75 °C for 1 hour. The residue was filtered and washed with aquadest until the pH was neutral, then dried in the oven at 80 °C for 5 hours. The third stage is deacetylation, the extracted chitin (residue from the second stage) was mixed with 45% NaOH solution (1:20) and heated at 140 °C for 1 hour. The residue was filtered and washed with aquadest until pH became neutral. Chitosan was dried in an oven at 80 oC for 5 hours [12].

2.2. Application of chitosan as a natural coagulant
The current study used three different samples, water with artificial turbidity, river water from the Mataram ditch, and batik wastewater. The location for taking river water is in the middle of the Mataram River, located in Yogyakarta. The batik wastewater was collected from batik industry at Rejodani, Sariharjo, Ngaglik, Sleman, Yogyakarta. The Scallop shell-based chitosansolution was made by following some steps. One gram of powdery chitosan was dissolved in 100 ml of 2% acetic acid, then stirred using a magnetic stirrer for 6 hours to ensure that the chitosan is completely dissolved.

The ability of the natural coagulant was compared with the performance of commercial coagulant (alum) in reducing the turbidity of water with artificial turbidity. The study was conducted in several different coagulant doses (100, 150, 200, 250 and 300 mg/L) and pH solution (5, 6, 7, 8 and 9) by using the jar test method. 500 mL of water sample were added with some doses of both coagulants (natural and commercial), mixing on 100 rpm for 1 minute and then continued with slow mixing at 60 rpm for
10 minutes. After the flocculation process is complete, the formed floc was allowed to settle for 30 minutes and the sample was analyzed immediately.

2.3. **Optimal dose of coagulant**

The jar test method has an important stage in determining the optimum coagulant dose. The first stage, dissolving coagulants with various doses specified, it is 100 mg / L, 150 mg / L, 200 mg / L, 250 mg / L, and 300 mg / L into a container containing 500 mL of sample water. Then do a fast mix (coagulation) at a speed of 100 rpm for 1 minute. The second stage is a slow mix (flocculation) to form the bigger flocks with a speed of 60 rpm for 10 minutes. The third stage is sedimentation for 30 minutes while the final turbidity is measured using a turbidimeter. those steps were to obtain the optimum coagulant dose in this study.

3. **Results and Discussion**

3.1. **Properties of water sample**

The research was started by analyzing the initial turbidity of the artificial turbidity sample, river water, and batik wastewater. This test is very important to know the properties of the sample before continuing to the next steps. The sample properties of the analysis results are shown in Table 1. The varying turbidity concentration of all samples is necessary to know the potential of the coagulant to be used in a variety of different concentration ranges.

| Type of sample          | Value | Unit | Method       |
|-------------------------|-------|------|--------------|
| Artificial turbidity    | 14    | NTU  | Turbidimetry |
| River water             | 81    | NTU  | Turbidimetry |
| Batik wastewater        | 1047  | NTU  | Turbidimetry |

3.2. **Optimum dose of chitosan for the artificial water turbidity**

An optimum dose of coagulant is required to achieve the best outcome from the removal of turbidity from water. The test result of turbidity reduction of artificial water turbidity with a variety of different coagulant doses is shown in Figure 1. It is shown that the optimum coagulant dose for alum and scallop shell-based chitosan is 150 mg/L with a turbidity reduction percentage of 100 percent from the initial concentration of 14 NTU becoming 0 NTU.

Based on Figure 1, when coagulants were applied at doses of 200 mg/L, 250 mg/L and 300 mg/L, the percentage of turbidity elimination decreased by 8-10% from the previous dose. Decreased elimination of turbidity was due to the addition of unnecessary coagulants. The coagulant will bind colloidal particles in water, and when the coagulant dose equivalent to the amount of colloid present in water, it will create another coagulant-derived colloid that will induce turbidity in water [13].

Because chitosan has a lot of nitrogen in its amine groups, amine and hydroxyl groups make chitosan more active. These properties make it mostly used as a coagulant in wastewater treatment. Chitosan can bind heavy metals because polyelectrolyte in chitosan has a negative charge while metal has a positive charge [14].

The principle of coagulation with chitosan is ion exchange. The amine salt formed due to the reaction of the amine and acid will exchange protons that are owned by heavy metals with electrons that are owned by nitrogen (N). Liquid waste containing heavy metals in reaction with chitosan, especially with its amine groups, will turn into a colloid called a floc that can settle in the bottom of the unit process.
3.3. Effect of pH on the coagulation process
The pH of the solution is one of the most significant variables in the method of coagulation of water and wastewater treatment. The characteristic of the coagulant is influenced by the pH of the solution due to the speciation of the aluminum which is usually the most dominant material of the coagulant [15]. The charge of the natural coagulant material is often influenced by the pH of the solution, where the acidic pH is normally positively charged [16], [17]. After finding the optimum dose for scallop shell-based chitosan and alum (150 mg/L), a pH change for chitosan and alum was made where the initial pH was 6. The pH change applied was pH variation with a pH spectrum of 5, 6, 7, 8 and 9. For optimum pH analysis, the turbidity will be determined after 30 minutes of sedimentation. The result of the coagulants process in this current study with different pH (5 to 9) is shown in Figure 2.

![Figure 2. Effect of pH on the effectiveness of reducing turbidity.](image)

Based on the results in Figure 2, the percentage of turbidity removal between alum and chitosan can be compared, according to pH conditions. Chitosan has an optimal turbidity removal at pH 7 and below (acidic), while alum coagulant has an optimum turbidity removal at pH 7 and above (alkaline).

3.4. Optimum dose of chitosan for river water
Chitosan-based scallop shell waste was used to remove the turbidity of river water. The results of the analysis are shown in Figure 3. In initial pH conditions at 7.6 (original pH of river water), the turbidity of the river water may be reduced with varying values depending on the difference in the dose of chitosan. Added chitosan at doses of 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L and 300 mg/L decreased...
turbidity of river water from 81 NTU into 26.24 NTU, 22.34 NTU, 23.82 NTU, 23.31 NTU and 22.50 NTU, respectively.

![Figure 3](image-url) Determining the optimum dose of chitosan in reducing turbidity in river water.

Based on Figure 3, the highest reduction in turbidity was obtained with the scallop shell-based chitosan at the dose of 150 mg/L. Even though the concentration of turbidity in the river water after coagulation by using this natural coagulant is still higher than standard (5 NTU based on Indonesian and WHO standard), however, in real water and wastewater treatment, the process will be followed by filtration in order to produce better water quality.

3.5. **Optimum dose of chitosan for batik wastewater**

The obtained natural coagulant was also employed to reduce the turbidity of batik wastewater and the results of this study are shown in Figure 4. It can be seen that the turbidity of batik wastewater can be reduced with different values according to the variation in the dose of scallop shell-based chitosan given. The chitosan doses of 100, 150, 200, 250, and 300 mg/L can reduce the turbidity of batik wastewater from 1047 NTU (initial turbidity) become 225, 210, 190, 167, and 132 NTU, respectively. Based on Figure 4, the increase of chitosan dose can increase the reduction of turbidity in batik wastewater samples, where the percentage of turbidity removal reached 87% at dose 300 mg/L.
Figure 4. Determining the optimum dose of chitosan in reducing turbidity in batik wastewater.

The results of the study had met the predetermined quality standard that is 200 NTU for batik wastewater based on DIY Governor Decree No. 7 of 2016 concerning Wastewater Quality Standards for the Batik Industry.

4. Conclusion
Based on the results of this study, the optimum dose of scallop shell-based chitosan was obtained at 150 mg/L that can reduce turbidity up to 100% for artificial turbidity, up to 72% for river water, and up to 87% for batik wastewater. This natural coagulant can reduce turbidity more effectively at a pH condition of 6 (acidic). The performance of scallop shell-based chitosan to reduce artificial turbidity, river water, and batik wastewater was similar to the commercial coagulant such as alum, making this natural coagulant a promising coagulant for water and wastewater treatment.

5. Conclusion
This study explains that CFD provides a very good contribution related to the calculation of resistance on trimaran ships, both conventional NPL and with Axe-bow modification. Ships with Axe-Bow modifications have a positive effect on trimaran resistance at S/L = 0.3 and S / L = 0.4 with an average drag reduction of 26.6%. This can occur because the Axe-bow modification is able to reduce wave generation to reduce the interaction between the hulls. The positive value of Axe-bow modification can be inputted and considered for the initial design of the ship.

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