Comparison of the Effectiveness of Natural Coagulant Performance on % BOD Removal and % COD Removal in Pharmaceutical Industry Waste

Agustin Maharani Z.P¹, Dwi Setiawan², Erlinda Ningsih³
Department of Chemical Engineering, Institut Teknologi Adi Tama Surabaya
e-mail : Erlindaningsih84@itats.ac.id

Abstract
Waste treatment can be done in various ways. One of the methods that can be used is the coagulation and flocculation method. The coagulant used can be either a chemical coagulant or a natural coagulant. Natural coagulants can be used in wastewater treatment for % removal of BOD and % removal of COD. By using moringa seed coagulant, it showed % removal of BOD of 90.12% and % removal of COD in the pharmaceutical industry waste a maximum of 71.23%. Through the use of tapioca starch coagulants, % removal of BOD and COD was 95.25% and 94.63%. The use of small crab chitosan coagulant showed % removal of both BOD and COD’s results was 32% and 31%.

Keywords: Coagulation, natural coagulants, pharmaceutical industry waste

I. INTRODUCTION
In this modern era, more and more industries have been established to meet people's daily needs. So that in this industrial competition, it causes a lot of environmental pollution from waste produced by both small and large scale industries. One of the many industries found in Indonesia is the pharmaceutical industry. Pharmaceutical industrial waste is one of the wastes that has the potential to pollute the environment, because the content of pharmaceutical waste is toxic, corrosive, reactive and flammable. This pharmaceutical industry waste can fall into the category of B3 waste (Hazardous and Toxic Materials). Many parties are aware of the dangers of this pharmaceutical waste, but there is still little processing of pharmaceutical waste. Therefore, it is necessary to treat waste in an easy and efficient way so that pharmaceutical waste disposal is in accordance with established wastewater quality standards.

Waste treatment can be done in various ways. The choice of method in the processing of pharmaceutical industrial waste can be done by considering the characteristics of the waste, environmental quality standards, and processing operational costs. Currently, many studies are being conducted to treat pharmaceutical waste using the coagulation-flocculation method. Where in the research of pharmaceutical industrial waste treatment, coagulants play an important role for an easy and efficient method of operation.

The coagulant used is a natural coagulant. Natural coagulants that are often used as coagulants include tamarind seeds, moringa seeds and chitosan. Tamarind seeds show results as a coagulant for the purposes of reducing the concentration of industrial dyes in tempe. Research (Hardi et al, 2017) shows that tamarind seed coagulant is able to provide % removal of COD, BOD and TSS in tempe waste of 82.6%, 78.5% and 86.4% with an effective dose of 150 mg / L. Research (Ramadhani et al., 2013) on tempe industrial waste obtained BOD removal efficiency of 82.62%, COD of 81.72% and TSS of 76.47%.

Apart from its use in the tempe industry, tamarind seeds are also used as a coagulant in the textile industry. Previous research (Martina et al, 2018) showed that tamarind seeds gave the highest concentration reduction at pH 4.5 and a dose of 3.68 mg / L with a decrease in dye for the textile industry by 94.29%. In a study (Ulwia and Rosdiani, 2017) using tamarind seeds for the tofu factory industry with BOD and COD removal results of 42% and 48% at a dose of 800 mg /
L. Moringa seeds are also often used in textile waste treatment, one of which is a coagulant for COD, BOD and TSS removal. Based on research that has been done (Irmayana et al, 2017)moringa seed coagulants can remove COD and BOD up to 104.96 mg / L and 20.52 mg / L in leather textile industry waste. In the study (Setyawati et al, 2019)showed the results of BOD and COD removal were 90.77% and 96.77% in tofu industrial waste treatment. Also for the tofu industrial processing researched by (Coniwanti, 2013), moringa seed coagulant can reduce COD content by 299 mg / L, TSS by 199 mg / L and turbidity by 52 NTU with an optimum dose of 1000 mg / L. (Rustiah et al, 2018) examined the coagulant of moringa seeds in laundry waste water with a decrease in COD content of 307.70 mg / L with a level of 0.7 grams and BOD 19.167 mg / L with a level of 2.4 grams. In the study (Bangun et al, 2013) the use of Moringa seeds at a dose of 5000 mg / L with 60 minutes of deposition can reduce the turbidity content by 77.43%, TSS by 90.32%, and COD by 63.26%. Meanwhile, according to other research (Meicahayanti et al, 2018) the use of chitosan in textile waste can reduce TSS by up to 89.55% at a dose of 150 mg / L. In the study (Pradifan et al., 2016) using chitosan can reduce the COD and TSS parameters of the semarangsingsosari channel water at an optimum dose of 200 mg / L with results of 75.63% and 80.23%. (Putri et al, 2015) examined the ability of chitosan to reduce COD content from 755.97 mg / L to 206.62 mg / L at a dose of 200 mg / L and turbidity from 516.20 NTU to 6.11 NTU at a dose of 200 mg / L on industrial laundry waste. In the study (Setiawan et al, 2017) chitosan coagulant had BOD and COD removal efficiency of 75% and 87.66% for treating textile liquid waste.

In this literature study, we wanted to know the performance of a better and more efficient coagulant between natural coagulants (Moringa seeds, tapioca flour, crab shell chitosan) for processing pharmaceutical industrial waste against% BOD removal and% COD removal.

II. RESEARCH METHODS

Coagulation Method

At the initial stage of the research, a literature study was carried out on the coagulation process. The working principle of coagulation is to destabilize the particles in the water so that they can be removed through the next separation process. The particles in water can be destabilized by the adsorption of ions or polymers which have opposite charges. Most of the pollutant particles in water such as acids, bacteria and sludge have a negative charge at a neutral pH or a pH range of 6 - 8. These particles can be destabilized using iron salts and organic cation polymers by charge neutralization. Organic cation polymers can be used as primary coagulants, however organic cation polymers are often used together with inorganic coagulants to form polymer bridges (Crittenden et al, 2012).

In general, the optimal dose of coagulant occurs when the surface of the particles is only partially covered. Polymers with a high density charge and with a low to moderate molecular weight are more easily adsorbed by negatively charged particles. Therefore, the optimal dose increase is proportional to the surface area of the particle concentration (less than 50%). The use of the correct coagulant dose will cause the polymer to be properly adsorbed and will neutralize pollutant particles to form floc (flocculation). However, if an excessive dose of coagulant is used, the particle charge will stabilize again(Crittenden et al, 2012).

Based on the literature studies that have been conducted, the coagulant dose is an important factor in the coagulation process. Apart from the coagulant dose, factors that affect the coagulation process are:
1. Coagulant dosage
2. Types of coagulants
3. pH
4. Mixing speed

Coagulation Method With Moringa Seed Coagulant

In the research of Etih Hartati, et al. (2008), the biocoagulant used was Moringa seeds in powder form. Previously, Moringa seeds are processed first. The peeled moringa...
seeds are mashed and heated at a temperature of around 60°C to remove moisture content, after that it is sieved in a size of 24 mesh, so that moringa seeds are obtained in powder form. The optimum dose used is 37,500 ppm with a stirring speed of 100 rpm for 10 minutes followed by 60 rpm for 15 minutes, observations were made for 3 x 24 hours.

The optimum pH of the Moringa seed bioaugulant is 8. After that, BOD and COD checks were carried out. The research with moringa seed coagulant was conducted by Nitesh Parmar and J.K Srivastava (2018), by processing 25 grams of crushed Moringa seeds into a powder measuring 28 mm. Moringa seed powder was then extracted using 1.5 liters of hexane solvent at a temperature of 65°C for 6 hours. The purpose of the extraction is to separate the oil from the Moringa seed powder which will be used as a coagulant. With an optimum dose of 100 mg / L, it is put into a beaker glass containing the sample solution. Stirring at a speed of 100 rpm for 2 minutes and followed by 20 rpm for 10 minutes, after that it is deposited for 30 minutes. Then filtered using filter paper.

**Coagulation Method With Tapioca Starch Coagulant**

In the research of Hesty Nuur Hanifah and Ju Hendra (2020), the processing of pharmaceutical industry waste uses a coagulant from tapioca flour. Pharmaceutical industrial waste is prepared in 250 ml beaker glass. The optimum pH is adjusted by adding 1N HCl to lower the pH, or adding 1N NaOH to raise the pH until pH = 11. The 2 mg / L tapioca starch coagulant is added to the pH-adjusted waste sample. Stirring is carried out at the optimum time, which is 15 minutes. Stirring is stopped and left for 30 minutes. After that, the BOD and COD checks were carried out using the UV Pastel tool.

**Coagulation Method Using Crab Shell Chitosan Coagulant**

Research conducted by Widyastuti Kusuma Wardhani, et al (2014) used crab shell chitosan as a natural coagulant in the processing of pharmaceutical industrial waste. The crab shell chitosan coagulant is processed first. The waste of chitin shells is washed and dried, then crushed in a blender. In the demineralization process, the crab shells were soaked in 2 N HCl solution for 48 hours. Change the HCl solution every 24 hours. Wash the crab shells with distilled water until a pH of 7.00. In the deproteinization process, soak the crab shells with 1 N NaOH solution for 12 hours. Heat the crab shells on the stove at 98°C for 36 hours.

Preparation of the dosage of the chitin in the crab biocoagulant was carried out by processing 1 gram of chitin dissolved in 100 ml of 85% phosphoric acid and obtained 1% chitin solution. Then the chitin solution was diluted with a 50 ml volumetric flask and a solution of 0.05% was obtained. A total of 0.05% chitosan biocoagulant solution was put into a beaker glass containing 1,000 ml of sample water. Performed with fast stirring of 100 rpm for 1 minute and 40 rpm for 20 minutes, and then deposited for 15 minutes.

**III.RESULTS AND DISCUSSION**

Based on the results of literature studies that have been carried out, natural coagulants that can be used in the processing of pharmaceutical industrial waste are: Moringa seeds, tapioca flour and crab shell chitosan. The effectiveness of natural coagulants can be assessed by the% removal of BOD and% removal of COD achieved in the coagulation process in pharmaceutical industrial waste. The effect of adding natural coagulants on BOD removal of pharmaceutical industry waste is shown in Figure 1.
Based on Figure 1, it is known that the results of research conducted by Nitesh Parmar and J.K. Srivastava (2018) using natural coagulants from moringa seeds provide a % BOD removal of 90.12%. These results were obtained from the use of a dose of 100 mg/L with a stirring speed of 100 rpm for 2 minutes and 20 rpm for 10 minutes with a settling time of 30 minutes. The% removal of BOD in the study of Hesty Nur Hanifah and Juhendra (2020) was 95.25% obtained by using tapioca flour coagulant with the use of a dose of 2 g/L and stirring using a magnetic stirrer for 15 minutes with a settling time of 30 minutes. Whereas in the study by Wardhani et al. (2014) using the crab shell chitosan coagulant was only able to provide a % BOD removal result of 32%. These results were obtained when using a dose of 0.05% by volume of waste by stirring at 100 rpm for 1 minute and 40 rpm for 20 minutes, and the settling time for 15 minutes.

The use of tapioca flour coagulant showed the most optimal% BOD removal results. The high% removal of BOD was obtained from the presence of hydroxyl (−OH), carboxyl (−COOH) and amide (−CONH2) groups. Carboxyl, hydroxyl, and amide groups are the constituent groups of organic polymers. The presence of carboxyl groups causes biocoagulants to be negatively charged, while amide groups cause biocoagulants to be positively charged. So it can be said that there are two different loads in tapioca flour (amphoteric) which will act as coagulation agents. Protein as a water-soluble natural polymer has properties such as polyelectrolytes and is positively charged so that it can bind to colloids and form floc that can settle. (Prihatiningtyas and E. Efendi J.A, 2018)[12].

In the study of Nitesh Parmar and J.K. Srivastava (2018) using a moringa seed coagulant showed a % BOD removal of 90.12% at a smaller dose (0.1 g/L) than the coagulant dose of tapioca flour (2 g/L). This is because the protein content in Moringa seeds is greater than tapioca flour. According to Setyawati, et al. (2018) 100 grams of moringa seeds contain 38.4 grams of protein. Meanwhile, according to Prihatiningtyas and E. Efendi (2018) the protein content in tapioca flour is only 1.1 grams per 100 grams of tapioca flour. So that in theory the moringa seed coagulant is more effective than the tapioca starch coagulant. But in this case the tapioca starch coagulant is more effective because of the use of a larger dose than the dosage used by the moringa seed coagulant.

The use of crab shell chitosan coagulant in the study of Wardhani et al. (2014) showed that % removal of BOD was 32% with a dose of 0.05% by volume of waste. The results of the crab shell chitosan coagulant showed that this coagulant was less effective for use in % BOD removal. The effectiveness of chitosan coagulant is influenced by the molecular weight of chitosan. According to Tsaih (2002) the molecular weight of chitosan is lower the higher the degree of deacetylation. The
A decrease in chitosan molecular weight also occurs due to polymerization caused by heating. In Wardhani's research, et al. (2014), the process of making chitosan, one of which is heating at 98°C for 36 hours, produces a degree of deacetylation of chitosan of 81.2%. Thus, the molecular weight of chitosan tends to be low. According to Tsaih (2002), low molecular weight reduces the effectiveness of chitosan as a coagulant. Because chitosan with low molecular weight takes longer to form macrofloc.

In addition to % BOD removal, the parameter used to determine the effectiveness of the coagulant was the % COD removal achieved. The effect of the addition of natural coagulants on the COD removal of pharmaceutical industrial waste is shown in Figure 2.

![Figure 2. Effect of natural coagulant over % removal COD](image)

Based on Figure 2, it is known that the results of research conducted by Etih Hartati, et al. (2008) using natural coagulants from moringa seeds gave COD removal of 71.23%. The results were obtained from using a dose of 37,500 ppm with stirring at 100 rpm for 10 minutes followed by 60 rpm for 15 minutes, leaving it for 3x24 hours. % COD removal in the study of Hesty Nuur Hanifah and Juhendra (2017) was 94.63% obtained by using tapioca flour coagulant with the use of a dose of 2 g / L and stirring using a magnetic stirrer for 15 minutes with a settling time of 30 minutes. Whereas in the study by Wardhani et al. (2014) using the crab shell chitosan coagulant was only able to provide a % COD removal result of 31%. These results were obtained when using a dose of 0.05% by volume of waste by stirring at 100 rpm for 1 minute and 40 rpm for 20 minutes, and the settling time for 15 minutes.

Based on research conducted by Etih Hartati, et al. (2008) moringa seed coagulant can provide a maximum % COD removal in pharmaceutical industry waste of 71.23%. This is evidenced by the results of % COD removal at doses less than 37,500 ppm, the amount of positive charge from biocoagulants cannot attract all colloids (negative charge) so that they cannot be bound and combined into floc. Likewise, doses above 37,500 ppm, there is an excess of positive charge so that the colloids cannot combine to form flocks. These two things cause the settling time to increase.

The use of tapioca flour coagulant in the research of Hesty Nuur Hanifah and Juhendra (2020) gave COD removal of 94.63%. According to Prihatiningtyas and E. Efendi (2018), high % COD removal is caused by the presence of an amide group which results in a biocoagulant with a positive charge. Thus, allowing the mechanism.

The decrease in heavy metal concentrations is due to the activity of natural coagulant amino acids which can adsorb and
form stable bonds between wastewater particles and natural coagulants. The existence of this stable bond allows deposition. The use of crab shell chitosan coagulant showed that % COD removal was not much different from the resulting % BOD removal, which was 31%. The chitosan produced in the research of Wardhani et al. (2014) has a low molecular weight caused by the heating process and the high degree of deacetylation. The low molecular weight of chitosan causes longer macrofloc formation. Thus, the effectiveness of the chitosan coagulant is not as good as the coagulant of moringa seeds and tapioca flour.

IV. CONCLUSION

From this literature study it can be concluded that the optimal results for % removal of BOD and % removal of COD with the use of tapioca flour coagulants. Tapioca flour coagulant was able to produce % BOD removal of 95.25% and % COD removal of 94.63%.

REFERENCES