The Effectiveness and Cost Optimization of Coagulant Aluminum Chlorohydrate (ACH), Aluminum Sulfate (AS), and Poly Aluminium Chloride (PAC) in Coagulation Process at The PT. Pupuk Sriwijaya (PT. Pusri) Utility Unit

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Abstract
PT. Pusri utilizes Musi River water as a source of process water. Colloidal particles suspended in Musi River water can cause blockage and build-up of scale on pipes and process equipment. Therefore, a good coagulation process is needed to reduce the content of colloidal solids suspended in water by using a coagulant. Coagulants that are often used for water treatment include ACH, AS, and PAC. The objectives of the study are to assess the effectiveness and to optimize the usage of the coagulant ACH, AS, and PAC on decreasing the turbidity of Musi River water sample as a raw water in utility unit of PT. Pusri. The coagulation process was carried out by varying the concentration of each coagulant and adding 0.1 ppm of coagulant aid for all samples. Fast and slow stirring was carried out each at a speed of 150 rpm 30 rpm for 10 minutes. From the experiments conducted, it was found that the most effective coagulants to be used were ACH and PAC with the addition of a smaller coagulant dose of 12 ppm to achieve the standard water quality used at PT. Pusri. Meanwhile, the use of AS has higher efficiency when compared to ACH and PAC because it is more cost effective.

Keywords
Coagulation, Coagulants, ACH, AS, PAC

1. INTRODUCTION
Water is needed in the industry to run industrial processes and activities. The use of water in the industry such as for process water, heating media, cooling media, raw materials production, drinking water, and daily necessities. Most of the water comes from various sources such as dug wells, drilled wells, springs, rivers, and the sea. Water used in industry has minimum specifications. Decreased water quality can affect the productivity, function, yield, carrying capacity, and capacity of water resources (Rosyidah, 2018). Turbid water such as river water must be treated first to meet the requirements for use as raw water. To meet the water needs in the factory PT. Pusri as one of the largest fertilizer factories in Indonesia, where Musi River water as a source of raw water. The water treatment unit at PT. Pusri uses coagulation and filtration processes to obtain filtered water. Coagulation and flocculation are one of the chemical processes used to remove suspended or colloidal contaminants where these colloidal particles cannot settle by itself and are difficult to handle by physical treatment (Ghermaout, 2020).

The coagulation process can be carried out through the stages of stirring between the coagulant and raw water and neutralizing the charge. The principle of coagulation is that in raw water there are solid particles that are mostly negatively charged (Prakash et al., 2014). These particles tend to repel each other so that they remain stable in suspended or colloidal forms in water. Neutralization of the negative charge of solid particles is carried out by adding a positively charged coagulant to the water followed by rapid stirring (Romadhon, 2016). Flocculation is the process of collecting particles with unstable charges which then collide with each other to form a collection of particles of larger size known as flocculants or flocs (Rusydi et al., 2017). In water treatment, coagulation and flocculation are still essential components of the overall suite of treatment processes (Rui et al., 2012). These processes are two interconnected processes using the addition of coagulant to form large flocs so that they are easy to precipitate (Khalid and Hind, 2016). Coagulant has
several functions, namely to reduce turbidity due to the presence of inorganic and organic colloid particles, reduce color by colloidal particles in water, pathogenic bacteria in colloidal particles, taste and odor caused by colloidal particles (Martina et al., 2018).

One of the chemical coagulants that are often used in industrial water treatment processes are aluminum-based coagulants such as ACH, AS, and PAC. Coagulant ACH serves to increase the size of colloidal particles and the formation of flocs so that the formed floc will be easier to settle. ACH can remove particles efficiently because it has a higher cationic charge density compared to other types of coagulants (Solrabi et al., 2018). PAC is an effective substitute for a solid alum because it results in a rapid coagulation process of water with different turbidity, generates less sludge, and also leaves less aluminum residue in treated water (Rahimah et al., 2016). PAC is a polymer aluminum which is a new type of coagulant as a result of research and development of water treatment technologies (Aziz et al., 2017). When compared with AS coagulant, PAC has several advantages, namely, it has low corrosivity, the floc produced is easier to separate, and the pH of the treated water is not too low when compared to AS (Murwanto, 2018). Other advantages of PAC coagulants are that PAC does not become cloudy when used in excess, sufficient base content will add hydroxyl groups in the air so that the pH drop is not too extreme, and PAC coagulants form flocs faster than ordinary coagulants (Rahimah et al., 2016). The coagulant agents, such as AS, are usually added during the initial stage of coagulation process, in order to enhance the removal of suspended solids, including colloidal particles, as well as of natural organic matter (Zouboulis et al., 2008). AS can be used for water purification through the process of coagulating dissolved and suspended solids in water so that it can be used for cleaning well water, as a cosmetic ingredient, certain dyes and tanning agents (Husaini et al., 2018). Turbidity reduction is often accomplished using chemical coagulants such as AS (Choy et al., 2014). AS is a coagulant that is widely used because it is more economical, easy to obtain for the market and easy to store, and can precipitate organic substances quickly.

The problem that usually occurs during the coagulation process is the length of time for the formed flocs to settle. This is because the flocs formed are still small and light in size, so the separation process becomes difficult (Yann et al., 2020). To speed up sedimentation and get clearer water, coagulant aid added. Coagulant aid serves to assist coagulation process. The coagulation process with the addition of coagulant aid can make the floc formed denser and shorten the settling time (Sillanpää et al., 2018). The coagulants aid are secondary coagulants that are added after the primary coagulants where the addition of coagulants is useful for accelerating hardening, formation, and deposition of flocs (Afdal and Fadhilah, 2020). Colloidal particles suspended in Musi River water can cause blockage and build-up of scale on pipes and process equipment. Therefore, a good coagulation process is needed to reduce the content of colloidal solids suspended in water by using a cost-effective coagulant. PT. Pusri is currently using ACH for the coagulation process in the utility unit of the Pusri III factory. Factors that greatly affect the quality of coagulation are the amount of coagulant and the type of coagulant used. The dose of coagulant and the type of coagulant used to affect the quality of the water produced (Nurjannah, 2015). Therefore, it is necessary to obtain the best type of coagulant and the optimum dose of coagulant injection in order to find the most suitable and cost-effective coagulant for use in the Pusri III factory.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Materials

This research was conducted to examine the effect of the coagulant concentration of ACH, AS, and PAC on the coagulation of Musi River water sample. The chemicals used are coagulant (ACH, AS, PAC), flocculant (Anion Flocculant Betagard 6100), Musi River water sample, and water. The raw water used was taken near the PT. Pusri Palembang pier.

2.2 Analysis/instrumentation

The tools used are jar test, beaker glass, analytical balance, watch glass, measuring pipette, stopwatch. Turbidity was measured by Benchtop HI88703 turbidity meter, and pH was determined by a Hanna pH meter.

2.3 Procedure

The coagulation process used ACH, AS, and PAC each as much as 10 g dissolved in 500 mL of water. Dissolving flocculants using the ratio used in the PT. Pusri III utility unit, which is 0.16667 g. The flocculant was dissolved with 500 mL of water and an additional dose of 0.3 mL of flocculant was added to 1 L of raw water. The addition of coagulant concentration was varied to 4-40 ppm. The coagulation process was carried out using fast and slow stirring. Fast stirring was carried out at 150 rpm and slow stirring at 30 rpm for 10 minutes. The coagulated water was analyzed to determine the pH value and turbidity.

3. RESULTS AND DISCUSSION

The coagulation process uses three types of coagulants namely ACH, AS, and PAC with the aid of anionic flocculant coagulant aid. Following are the results of the analysis of Musi River water sample before and after the coagulation process using ACH, AS, and PAC as coagulant.

3.1 Effect of Coagulants on Decreasing Turbidity

The coagulation process using ACH coagulant was carried out by varying the concentration of the addition of ACH as much as 4-40 ppm. The effect of ACH coagulant on decreasing turbidity can be seen in Figure 1.
The turbidity value using ACH coagulant decreased with increasing ACH concentration. The lowest turbidity value occurred with the addition of ACH with a concentration of 16 ppm with a turbidity value of 0.73 NTU. From the graph in Figure 1, the optimum concentration range for adding ACH coagulant is between 8-12 ppm. The addition of ACH with a concentration greater than 16 ppm can increase the turbidity value. This is because the addition of excessive ACH will cause more floc to be formed, so that the turbidity value becomes high. This is based on economic considerations because the addition of ACH coagulant at a concentration of 12 ppm has fulfilled the quality standards of the coagulation process at the water treatment unit at PT. Pusri so the addition of higher concentration of ACH is not recommended.

The coagulation process using AS as a coagulant was carried out by varying the concentration of AS as much as 8-40 ppm. The effect of AS coagulant on decreasing turbidity can be seen in Figure 2.

The turbidity value of coagulation using AS coagulant decreased with increasing AS concentration. The lowest turbidity value occurred with the addition of AS with a concentration of 20 ppm with a turbidity value of 0.76 NTU. The addition of AS with a concentration greater than 20 ppm can increase the turbidity value. The addition of excessive AS will cause an increase in turbidity due to the excessively formed floc (Rosariawari and Mirwan, 2010). Based on the graph in Figure 2, the most optimum concentration range for adding AS coagulant is between 16-20 ppm. This is because the formed floc has settled, so the turbidity value has decreased significantly. Another consideration is based on economic considerations, because the addition of AS coagulant above 20 ppm results in higher turbidity values and the use of AS in larger quantities is not cost effective.

The coagulation process using PAC coagulant was carried out by varying the concentration of PAC as much as 8-40 ppm. The effect of PAC coagulant on decreasing turbidity can be illustrated in Figure 3.

The turbidity value of coagulation using PAC coagulant decreased with increasing PAC concentration. The lowest turbidity value occurred with the addition of PAC with a concentration of 16 ppm with a turbidity value of 0.36 NTU. From the graph in Figure 3, the optimum concentration range for adding PAC coagulant is between 8-12 ppm. PAC coagulant added with a concentration of 12 ppm shows the turbidity value reached the quality standard for the treatment process in the utility unit of the Pusri III factory, which is 1.64 NTU. The addition of PAC with a concentration greater than 16 ppm can increase the value of turbidity caused by the number of cations added more than required for floc formation. Where the colloidal particles absorb excess cations which make the colloidal particles become positively charged and there is a repulsion between the particles resulting in floc deflocculation which increases the turbidity of the solution (Margaretha et al., 2012). Another consideration is based on economic considerations where the concentration of the addition of PAC coagulant above 16 ppm will result in higher turbidity and it will not efficient.
3.2 Effect of Coagulant on pH Value

In addition to turbidity, pH also affects the addition of coagulant. The indicator of a solution to determine the level of acidity formed can be seen from the pH value. The formation of the floc is greater than the size and weight, causing the floc to settle. The formation of floc which tends to decrease will decrease the pH value.

ACH is the most concentrated dissolved aluminum-based coagulant available and has the highest basicity (Naceradska et al., 2019). The effect of increasing the amount of ACH coagulant on the pH value is shown in Figure 4. The Figure 4 shows that after the addition of ACH coagulant the pH value of the sample increased and decreased from the initial sample’s pH value.

The decrease in the pH value is caused by the formation of acidic compounds formed from hydrogen ions. Meanwhile, the increase in pH value after the addition of coagulant occurred due to the excess of aluminum hydroxide compound which decomposed into \( \text{Al}^{3+} \) and 3OH\(^-\) (Makki et al., 2010). Excess hydroxide compounds cause the pH of the water to increase. Furthermore, the pH of the water that increased became stable this was due to the amphoteric nature of aluminum hydroxide. Amphoteric properties make aluminum can act as an acid or base in that aluminum hydroxide can work as a buffer to withstand changes in pH in the effective pH range of 6 which causes the pH to become stable (Altaher et al., 2016). The coagulation reactions that occur in the addition of ACH coagulant are as follows Equation 1:

\[
\text{Al}_2(\text{OH})_3\text{Cl} + \text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{H}^+ + \text{Cl}^- \quad (1)
\]

The addition of AS coagulant to the sample causes the release of a hydrogen ion in each hydrogen group. This hydrogen ion will cause a decrease in the pH value. A decrease in the pH value that occurs causes the water to become more acidic. Figure 5 shows the effect of the addition of AS on the pH value.

The addition of AS coagulant resulted in a decrease in the pH value compared to the pH value before the addition of the coagulant. The pH value tends to decrease after the addition of AS because the \( \text{H}^+ \) ion produced after the AS reacts with water. The decrease in pH that occurs is also because AS has acidic properties and when reacted with water will form \( \text{H}_2\text{SO}_4 \) compounds which reduce the pH value of water (Aziz et al., 2007). Hydrolysis of Al atoms in water can be described by the following Equation 2 for the reaction of AS:

\[
\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 6\text{H}^+ + 3\text{SO}_4^{2-} \quad (2)
\]

The release of \( \text{H}^+ \) ions in this reaction causes the pH of the solution to decrease. The reaction releases of \( \text{H}^+ \) ions as much as 6\( \text{H}^+ \), so that the pH value after the addition of coagulant will become more acidic. The high dose of AS coagulant in the sample causes the release of \( \text{H}^+ \) ions that will occur more and more, so that the pH of the water decreases.

In the coagulation process using PAC coagulants compared to ordinary coagulants, flocs will form more quickly.

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The aluminate active group binds to colloidal particles and the presence of a strong polyelectrolyte group polymer chain will bind the particles so that the floc will solidify faster and formed faster (Lin et al., 2017). The molecular weight of the particles will increase due to the addition of hydroxyl groups into the hydrophobic colloidal chain (Yan et al., 2008). The effect of increasing the amount of PAC coagulant on the pH value can be seen in Figure 6.

In Figure 6 it can be seen that after the addition of PAC coagulant the pH value tends to decrease even though at the beginning of the addition the pH value has increased compared to the pH value in the initial sample. A decrease in the pH value of the PAC coagulant occurs when the coagulant reacts with water resulting in a hydrolysis reaction that produces free hydrogen ions (Huang et al., 2013). The more the addition of PAC coagulant, the greater the decrease in pH that occurs. The number of bound H\(^+\) ions causes the pH of the solution to be low (Kumar and Balasundaram, 2017). Optimum use of PAC coagulant in the pH range 6-9. The coagulation reactions that occur in the addition of PAC coagulant are as follows Equation 3:

\[
\text{Al}_2(\text{OH})_3\text{Cl}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}^+ + 3\text{Cl}^- \quad (3)
\]

The hydrolysis reaction of adding PAC produces three H\(^+\) ions. The hydrogen ions produced were less than the AS coagulant, so the PAC coagulant had little effect on decreasing the pH (Daryabeigi Zand and Hoveidi, 2015).

### 3.3 Estimated Optimal use of Each Coagulant

At present, the coagulant used in plant III of PT. Pusri is ACH. Calculation of the amount of coagulant needed is carried out using data on water production capacity in the utility unit of plant III of PT. Pusri. The estimated price of each coagulant is calculated using the optimum concentration dose of coagulant addition. The water production capacity in PT. Pusri’s plant III utility unit is 660 m\(^3\) per day. The results of the estimated cost for each of the coagulants used can be seen in Table 1.

It is estimated that the cost of using alum coagulant is the cheapest compared to PAC and ACH. This is influenced by the market price of each coagulant. The price of AS coagulant is cheaper than PAC and ACH. The cost of using AS coagulant is IDR 28,512,000 per year. Where the expenditure is quite far, namely IDR 10,656,000 when compared to PAC and IDR 26,886,816 with ACH coagulant. Based on the effectiveness of the use of coagulants, the ACH and PAC coagulants are better than AS. The use of ACH and PAC coagulants was less than that of AS coagulants. ACH coagulant has more aluminum content than AS and PAC. ACH coagulant contains 23-24\% Al\(_2\)O\(_3\) while alum and PAC contain 7.5-8\% and 10-11\% Al\(_2\)O\(_3\) respectively (Gebbie, 2006). Aluminum compounds function to destabilize the negative charge on suspended solids in river water sample so that the more of Al\(_2\)O\(_3\) content, the more colloids are destabilized.

When aluminum is added to water, the Al cations on the aluminum undergo a series of hydrolysis reactions to form other dissolved Al species or aluminum hydroxide precipitates. The dissolved Al species formed are in the form of monomers and because some of them are positively charged they can neutralize the negatively charged surface of colloidal particles, allowing the coagulation process to occur. There are four species of Al that form in the hydrolysis reaction of aluminum, namely Al\(^{3+}\), Al(OH)\(^{2+}\), Al(OH)\(^{3+}\), dan Al(OH)\(^{4-}\). Species formation on aluminum is slightly different from that of PAC. In aluminum, only monomer species are formed while in PAC, in addition to monomers, polymeric cations are also formed, which is dominated by Al\(_2\)O\(_4\)(OH)\(_{2+}\) so that less coagulant is needed to destabilize suspended solids than alum coagulant (Sutapa, 2014). The use of alum coagulant produces water with a higher pH so it requires the addition of more NaOH than the use of ACH and PAC because OH\(^-\) ions can neutralize H\(^+\) ions, so that stability can be maintained and does not occur clumping. The addition of more NaOH increases production costs in the coagulation process using alum.

| Coagulants | ACH | AS | PAC |
|------------|-----|----|-----|
| Optimum concentration (ppm) | 12  | 20 | 12  |
| Price/kg or L       | IDR 14,500 | IDR 6,000 | IDR 14,000 |
| Needs/month         | 237.6 L    | 318.384 kg | 237.6 kg |
| Cost/month          | IDR 4,616,568 | IDR 2,376,000 | IDR 3,326,400 |
| Cost/year           | IDR 55,398,816 | IDR 28,512,000 | IDR 39,168,000 |

4. CONCLUSIONS

The decrease in turbidity occurs as the concentration of each coagulant increases until the lowest value decreases in turbidity and increases due to the addition of excess coagulant. The addition of coagulant tends to reduce the pH value of the sample due to the formation of H\(^+\) ions. PAC and ACH coagulants have better effectiveness at a concentration of 12 ppm than AS due to the addition of less coagulant to achieve water turbidity quality standards and the decrease in pH is not too low which fulfil the standard of utility unit in PT. Pusri.
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