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Determination of coagulant type and dosage in fertilizer industry wastewater treatment

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ABSTRACT

Fertilizer Industry produces wastewater which mostly contains fluoride. The wastewater has potential to be reused as raw water for the scrubbing process, even though it has not been utilized yet. The reduction of fluoride can be done by adding aluminum sulfate, quick lime, and PAC. The aim of this study was to determine the optimum dose of the aluminum sulfate as the main coagulant and quick lime or PAC as a coagulant aid to produce water for the scrubbing process. The optimum dosage was determined by the 2-stages of jar test method with the addition of variation in the concentration of coagulant and stirring at constant speed. The addition of aluminum sulfate as main coagulant and quick lime as coagulant aid at concentration of 50 – 60 mg/l gave the highest fluoride reduction efficiency.

Key words : *Jar test, Coagulant, Fertilizer industry wastewater, Scrubbing.*

Introduction

The main components of fertilizer industry wastewater contain of Nitrogen, Fluoride, Phospate, and Solid Particles (Gypsum) (Kusmayanti and Febriyani, 2013). The reduction of fluoride levels in water can be done by adding aluminum sulfate, quick lime, and PAC (Riskianto *et al.,* 2016). The fertilizer industry wastewater also contains Total Suspended Solid (TSS) which causes water turbidity. Suspended solids consist of particles that are smaller in size and weight than sediment, for example, clay, certain organic materials, cells of microorganisms, and so on. The suspended solid will reduce the penetration of light into the water which affects the oxygen regeneration by photosynthesis (Fardiaz, 2006).

The addition of PAC and quick lime can not only reduce the fluoride content but also reduce the Total Suspended Solid (TSS) content in wastewater (Tandiarrang *et al.,* 2016). The decrease in TSS content also affects the decrease in COD content. Wastewater test results fluctuate because they are influenced by the production process which is carried out depending on which factory unit is carrying out the production process (Arum, 2018).

Various previous studies have been conducted to analyze the factors and the appropriate method to reduce the COD, fluoride, TSS content and to neutralize pH. The factors include the addition of coagulants.

The fertilizer wastewater has not been utilized even though it has the potential to be reused as raw water for the scrubbing process for the wet scrubber unit. The effluent wastewater is needed to meet the standard for the raw water scrubbing process. The aims of this study is to analyze the effect of adding aluminum sulfate, quick lime, and PAC to manage pH stability in a neutral state and reduce fluoride and TSS levels in fertilizer wastewater which can be reused as raw water in the wet scrubber unit. Reduction of fluoride and TSS levels in wastewater is needed so as not to clog the spray flow in the wet scrubber. Laboratory-scale research is needed as a consideration before it is applied on a field scale. Further study is needed regarding the removal of fluoride and TSS from wastewater by utilizing coagulant aid, namely PAC or quick lime.

Materials and Methods

Data Collection

The study was conducted to analyze the ability of PAC and quick lime to reduce COD, fluoride, turbidity, and TSS, so that wastewater can be reused into raw water for the scrubbing process. The data collected was a primary data. Primary data were used to determine the changes that might occur after the addition of aluminum sulfate, PAC, and quick lime coagulant treatment.

Sampling was carried out to determine the quality of wastewater. The sample was taken by using the grab sampling method which refers to the SNI 6989.59-2008 guidelines. The sampling location is conducted at the Fertilizer Industry Factory. Sampling was conducted when the unit is operating normally to obtain the wastewater quality test results with a neutral pH. Sampling was carried out three times at the same hour and on different days. The wastewater samples were then taken to the laboratory for quality analysis. The parameters analyzed were COD, TSS, fluoride, turbidity, and pH.

Coagulant Stock

The aim of this study was to determine the appropriate type of coagulant and its optimum dose to meet the water criteria that have been determined for the scrubbing process, at an economical cost. The coagulation process which was carried out twice that went well will able to reduce turbidity, COD, and TSS. F and TSS parameters are the main focus in this research because these parameters still exceed the water criteria for the scrubbing process. This experiment used the jar test method and the coagulants used were aluminum sulfate as the main coagulant and quick lime and PAC as the coagulant aid (Table 1).

The first step is to make a coagulant stock solution with a concentration of 10,000 mg/l. The stock coagulant solution is made by weight according to certain calculations which are then dissolved in 1 liter of distilled water and stirred until the solution is homogeneous (Table 2).

Then the next step is to do a jar test. The first thing to do is to determine the dosage range for each coagulant. The volume of stock solution to be added is calculated to match the desired concentration. Then, check the pH and ensure that the pH is under conditions that do not fluctuate and meets the pH requirements so that the coagulant can work optimally. In this experiment, the lowest pH was found in the fourth sampling result, namely 5.8, therefore it was necessary to increase it to 8 by adding $CaCO_3$. This also applies to the results of the quality of treated water that has not reached pH 8.

Table 1. Specifications of Chemicals Used

Chemicals	Form	Purity(%)	Price perkg
Aluminum Sulfate	Fine Powder	17%	Rp 10.000
Quick Lime	Fine Powder	80%	Rp 5.000
PAC	Fine Powder	30%	Rp 20.000
Calcium Carbonate	Fine Powder	70%	Rp 3.000

Table 2. Chemicals Need as Stock Solutions

No	Coagulant	Content (%)	Stock Concentration (mg/l)	Required Weight (g)
1	Aluminum Sulfate	17	10.000	58.82
2	Quick Lime	80	10.000	12.50
3	PAC	30	10.000	33.33
4	Calcium Carbonate	70	10.000	14.29

For the preparation of $CaCO_3$stock solutions, it has the same method as for making coagulant stock solutions. The purity of $CaCO_3$used is 70%, so need to dissolve 14.29 g of $CaCO_3$in 1 l of distilled water to obtain a stock solution of $CaCO_3$with a concentration of 10.000 mg/l.

Determination of Coagulant and Its Dosage

The variables in this study were the type of coagulant aid and its doses. The initial dose to be added is in the range of 30 mg/l-80 mg/l for the main coagulant and coagulant aid. Then determine the optimum dose for each coagulant for the wastewater. The doses variation of coagulant were shown in Table 3.

For the jar test experiment, firstly, add the aluminum sulfate as the main coagulant with an additional dose of 30 mg/l-80 mg/l. Then, stir the sample solution using a jar test with a speed of 200 rpm for 2 minutes as a flash mix.

Results and Discussion

Data Collection

Wastewater characteristics data obtained from sampling which conducted on Monday, 18 November 2019, Tuesday, 19 November 2019, Wednesday, 20 November 2019, Thursday, 19 December 2019, and Friday, 27 December 2019. The analysis results show that the quality of the wastewater has not met water criteria for the wet scrubber unit for the scrubbing process. Table 4 describe the characteristic of fertilizer wastewater for each sampling.

In the jar test experiment, the highest and lowest sample quality results were taken, namely, the first sampling results and the fourth sampling results to obtain the range of costs required for treatment.

Determination of the Type and Optimum Dosage of Coagulants

Highest Concentration Sample with Aluminum Sulfate and Quick Lime Coagulant

In the first jar test experiment, the highest quality results were taken, namely the first sampling results with an initial pH of 7.7. In this sample, there is no need to add CaCO3 because it already meets the optimal pH range for the use of coagulants (5,5-8) (Schulz and Okun, 1984). The results of the jar test experiment using aluminum sulfate coagulant and quick lime coagulant can be seen in Figure 1.

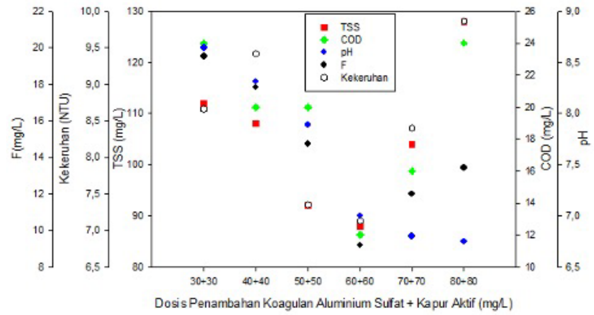

Fig. 1. First Jar Test Results with Aluminum Sulfate and Quick Lime Coagulant

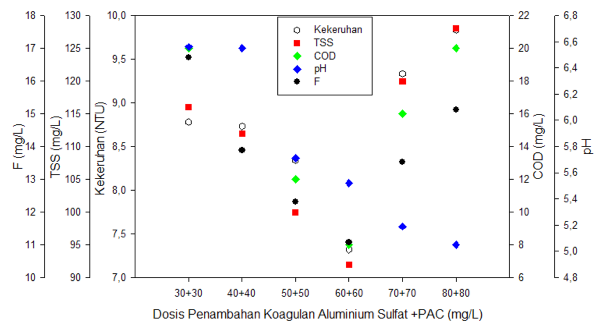

Fig. 2. Second Jar Test Results with Aluminum Sulfate and PAC Coagulant

Highest Concentration Sample with Aluminum Sulfate and PAC Coagulant

The second jar test experiment used the same sample and the same treatment as the first jar test experiment. The results of the jar test experiment using aluminum sulfate coagulant and Poly Alumi-

Table 3. Variation of Coagulant Dosage Addition

No	Coagulant	Dosage (mg/l)					
		I	II	III	IV	V	VI
1	Aluminum Sulfate	30	40	50	60	70	80
	Quick Lime	30	40	50	60	70	80
2	PAC	30	40	50	60	70	80
	Calcium Carbonate	30	40	50	60	70	80

num Chloride (PAC) coagulant can be seen in Fig. 2.

Lowest Concentration Sample with Aluminum Sulfate and Quick Lime Coagulant

The third jar test experiment used the sample with the lowest quality, namely the sample in the fourth sampling with an initial pH characteristic of 5.8. The pH of the sample needed to be increased to meet the optimum pH range for the use of coagulants (5-8) by adding $CaCO_3$. In this sample, it is necessary to add 33.3 mg/l of $CaCO_3$ to increase the pH to 8.

The characteristics of wastewater after being given $CaCO_3$ for turbidity, TSS, COD, pH, and F parameters in a sequence are 212 NTU, 172 mg/l, 51 mg/l, 8, and 38.92 mg/l. The results of the jar test experiment using aluminum sulfate coagulant and quick lime coagulant can be seen in Fig. 3.

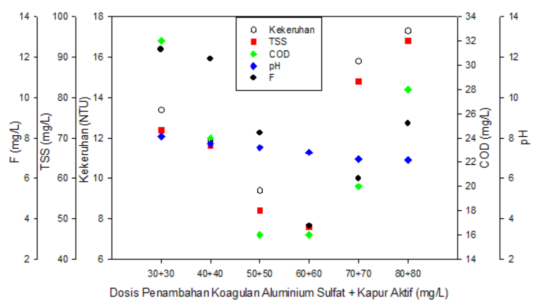

Fig. 3. Third Jar Test Results with Aluminum Sulfate and Quick Lime Coagulant

Lowest Concentration Sample with Aluminum Sulfate and PAC Coagulant

The fourth jar test experiment used the same sample and the same treatment as the third jar test experiment. The results of the jar test experiment using aluminum sulfate coagulant and Poly Aluminum Chloride (PAC) coagulant can be seen in Fig. 4.

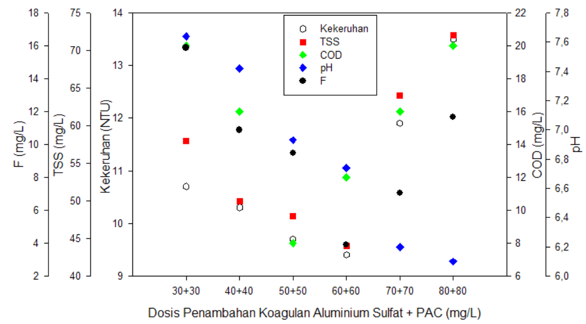

Fig. 4. Fourth Jar Test Results with Aluminum Sulfate and PAC Coagulant

Results of Type and Optimum Dosage of Coagulants Determination

The results of determining the optimum dose of main coagulant and coagulant aid along with the percentage removal in the parameters of treated water can be seen in Table 7 and 8.

Based on the jar test results, the most effective coagulants for treating treated water are aluminum sulfate main coagulant and coagulant aid quick lime. In this case, the addition of coagulant aid is needed because the pH will decrease drastically if only use aluminum sulfate. Besides being able to reduce the parameters of TSS, turbidity, COD, and F, the addition of coagulants can also cause a decrease in pH. The decrease in pH is also influenced

Table 4. The Characteristic of Fertilizer Wastewater Sampling

No	Parameter	Unit	Criteria	Number of Sampling				
				1st	2nd	3rd	4th	5th
1	pH	-	6 – 9	7.7	7.5	8	5.8	7.13
2	TSS	mg/l	100	376	132	114	76	164
3	COD	mg/l	30	60	24	28	34	44
4	Turbidity	NTU	-	183	88.2	75.5	38.6	75.5
5	F	mg/l	10	94.40	71.54	96.94	38.92	88.32

Table 7. Determination of the optimal dose of treated water coagulant in the first sample

No	Coagulant	Dosage (mg/l)	Turbidity	TSS	COD
1	Aluminum Sulfate	60	96,10%	76,60%	80%
	Quick Lime	60			
2	PAC	60	96%	75,53%	86,67%
	Calcium Carbonate	60			

Table 8. Determination of the optimal dose of treated water coagulant in the second sample

No	Coagulant	Dosage (mg/l)	Turbidity	TSS	COD
1	Aluminum Sulfate	60	96.72%	83.72%	69.81%
	Quick Lime	60			
2	PAC	60	95.95%	74.42%	85.19%
	Calcium Carbonate	60			

by the type of coagulant. Coagulants that react with wastewater can release H+ ions and cause the atmosphere to become acidic. Each type of coagulant has a certain pH range to work optimally. Thus, it is important to adjust and control the pH of the solution in the coagulation-flocculation method of waste treatment (Riskawanti *et al.,* 2016).

In the first sample, the addition of the main coagulant aluminum sulfate and coagulant aid quick lime with a concentration of 120 mg/l had an initial characteristic pH of 7.7 then decreased to 7. Whereas in the second sample, the addition of the main coagulant aluminum sulfate and coagulant aid quick lime with a concentration of 120 mg/l has an initial characteristic pH of 5.8 then increased to 8 by adding $CaCO_3$then decreased to 7.29.

Then the decreased pH of the main coagulant aluminum sulfate and coagulant aid PAC, in the first sample, has an initial characteristic pH of 7.7 then increased to 8 using $CaCO_3$ then decreased to 5.92.

Whereas in the second sample, the addition of the main coagulant aluminum sulfate and coagulant aid PAC with a concentration of 120 mg/l had an initial characteristic pH of 5.8 then increased to 8 using $CaCO_3$ then decreased to 5.52.

Based on the experiment above, the addition of coagulant aid quick lime does not experience a significant decrease in pH, because quick lime (CaO) in a water mixture will form a calcium hydroxide ($Ca(OH)_2$) compound which has alkaline properties and breaks down into two ions, namely ion OH^- and ion Ca^{2+} in water (Ravina, 1993). The hydroxide ion (OH^-) will increase the pH of the wastewater. The reaction is as follows:

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

Quick lime serves to make aluminum sulfate coagulants more effective in alkaline conditions. This can happen because when in an alkaline atmosphere, Al^{3+} in water will be hydrolyzed to form a positive complexion, this ion can absorb the surface of negative suspended particles (Jiao *et al.,* 2015). For the turbidity parameter, it is very closely related to suspended substances, because suspended substances in water are the cause of turbidity. The suspended substances in the water consist of organic or inorganic materials in the form of fine sand and natural mud. The suspended substances that are present in the water are floating in the water. The decrease in turbidity concentration is caused by the coagulation process where this process creates collisions between colloids and suspended particles which then form clots and are separated through the sedimentation process (Sarwono *et al.,* 2017).

For COD parameters, the highest removal efficiency was found in the addition of main coagulant aluminum sulfate and coagulant aid PAC. This is because the PAC coagulant is an organic polymer. If the coagulation mechanism is dominated by polymer bridges, the efficiency will increase with the addition of molecular weight. The increase in molecular weight and decrease in dissolving properties will be very large if there is the use of molecular compounds. Polymer chemicals are often used as coagulants in the coagulation process, polymers serve to help form macro flocs after destabilization, and the formation is caused by coagulants (Lofrano *et al.,* 2006). Hydrolysis of pH causes Al^{3+} ion in the coagulant solution to be hydrated (Sianita and Nurchayati, 2009). The compounds that will be formed have a positive charge and can react with pollutants such as colloids. The reaction is as follows:

$$[Al(H_2O)_6]^{3+} \longrightarrow [Al(H_2O)_5OH]^{2+} + H^+$$

$$[Al(H_2O)_5OH]^{2+} \longrightarrow [Al(H_2O)_4(OH)_2]^+ + H^+$$

$$[Al(H_2O)_4(OH)_2]^+ \longrightarrow [Al(H_2O)_3(OH)_3] + H^+$$

sediment

$$[Al(H_2O)_3(OH)_3] \longrightarrow [Al(H_2O)_2(OH)_4]^- + H^+$$

soluble

In the first stage, a compound with 5 water molecules and 1 hydroxyl group is formed whose total charge will drop from +3 to +2. If the pH in the solution continues to rise until it reaches the optimum pH, a second stage reaction will occur in which a compound that has 4 water molecules and 2 hydroxyl groups is formed. A solution with a pH >6 will form a neutral metal compound $Al(OH)_3$ which is insoluble, has a large volume, and can settle as a floc. At pH >7.8, a compound $[Al(H_2O)_2(OH)_4]$ or $Al(OH)_4$ will form, which is a compound with a negative charge and can dissolve in water. For this reason, in the coagulation process, pH control is needed so that the coagulant can work optimally so that it can precipitate the pollutants you want to remove. For pH parameters, the coagulation process using aluminum sulfate coagulant causes the release of one hydrogen ion for each hydrogen group that has been produced. The hydrogen ion that has been generated causes a significant decrease in pH so that the treated water becomes more acidic. This can be seen from the following reaction:

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

$$3H_2SO_4 \longrightarrow 6H^+ + 3SO_4^{2-}$$

From the above reaction, it can be seen that during hydrolysis, aluminum sulfate in water will release H+ ions as much as $6H^+$. Whereas in the PAC hydrolysis reaction, only $3H^+$ ions were released (Budiman, 2008). The addition of lime was chosen as a stabilizer for the pH value because the presence of Ca^{2+} ions in $Ca(OH)_2$ in excess conditions can form precipitates with other substances that have a negative charge (Hartati and Karnaningrum, 1993). The calcium in lime can be used to obtain the alkalinity of the solution required for pH control. The reaction of adding lime to control the pH value is based on the reaction:

$$Ca(OH)_2 + CO_2 \longrightarrow Ca(HCO_3)_2$$

The optimum dose of lime to raise the pH is at the saturated concentration. It results in a fairly good increase in pH value because, in the establishment of saturated lime, the amount of substance added is more, so the amount of substance dissolved in the lime solution is more. For parameter F, the highest removal efficiency is found in the addition of main coagulant aluminum sulfate and coagulant aid quick lime. This is because fluoride is usually removed by aluminum coagulants through precipitation with metal-hydroxide (Bratby, 2016). Fluoride can be removed with aluminum sulfate, but with the presence of quick lime as a defluoridation agent which acts as an 'assistant' to aluminum sulfate, the fluoride reduction process can take place more optimally. The reaction of reducing fluoride by aluminum sulfate and quick lime is as follows (Benefield and Morgan, 1999):

$$Al_2(SO_4)_3.14.3H_2O + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + 14H_2O$$

$$Ca(OH)_2 + 2HF \longrightarrow CaF_2 + 2H_2O$$

Conclusion

Based on the experiments and analyzes that have been conducted, it can be concluded that:

1. The optimum dose of adding the main coagulant aluminum sulfate in the jar test experiment to process Wastewater into raw water in the scrubbing process is 50 mg/l-60 mg/l.
2. The optimum dose for the addition of quick lime coagulant in the jar test experiment to process Wastewater into raw water in the scrubbing process is 50 mg/l-60 mg/l.

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