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The Effectiveness of Polyaluminium Chloride (PAC) As Coagulant to Treat Tannery Waste

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Abstract

α Research on the effectiveness of PAC coagulants for processing tannery waste was carried out to determine the optimum pH and determine the % effectiveness of PAC in reducing BOD, COD, chromium, TSS, sulfide, ammonia and pH in leather waste. The test jar method is carried out with a beaker filled with 300 mL of liquid waste each. A series of test jar experiments using a flocculator with pH variations, namely 4, 5, 6, 7, 8, 9 with fast stirring at 100 rpm for 2 minutes, and slow stirring at 25 rpm for 15 minutes. Dose variations were carried out with doses of 25 ppm, 50 ppm, 75 ppm, 100 ppm, 125 ppm. Determination of the optimum pH is done by measuring the final turbidity value. The optimum pH value for processing tannery waste with PAC coagulant is pH 8. The dose of PAC in reducing turbidity was greatest at a dose of 125 ppm. The effectiveness of 125 ppm PAC can reduce BOD 32.44 %, COD 12.23%, chrome 94.86%, TSS 91.62%. PAC coagulant with a dose of 125 ppm in leather processing waste increased the sulfide value from 103 ppm to 134 ppm and ammonia from 72 ppm to 134.11 ppm.

Keywords : tannery waste, coagulation, PAC, BOD, COD, chromium, TSS, ammonia, sulfide

1. Introduction

The leather tanning process is a process of stabilizing the leather so that it is resistant to physical, chemical, and biological attacks. The leather tanning process is conducted through 4 main process stages, i.e. beam house operation (BHO), tanning, post-tanning, and finishing. Those processes produce solid and liquid waste. The leather tanning industry produces 29.3 m^3 of liquid waste and 1.75 tons of solid waste from 1.5 tons of salted leather [1]. According to Bhargavi et al [2] and Sekaran et al [3], 1 kg of rawhide will produce 30-35 liters of liquid waste and 0.7 kg of solid waste. Tannery liquid waste contains organic pollutants, metals, dissolved solids, acids, and bases. Since the waste still contains high pollutants, waste processing is required to reduce pollutants content (physical, chemical, biological), especially in the liquid waste, so that it is safe for the environment.

Waste processing is based on 3 processes, namely physical, chemical, and biological processing. Physical processing is carried out using the principles of physical laws, for example: screening, sedimentation, and filtration. The main principle of physical wastewater treatment is to remove suspended solids in the wastewater [4]. Screening is the initial process of filtering solid particles from the liquid. Sedimentation aims to separate particles in the solution based on gravitational forces [5]. Chemical processing is carried out by adding chemicals, for example, coagulation, flocculation, and adsorption. Biological processing is carried out using microorganisms. Examples of biological processes are

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aerobic, anaerobic, and phytoremediation. The main purpose of the biological treatment is to reduce or eliminate the organic material content in the wastewater. Biological treatment is also can be conducted to remove nitrogen and phosphorus from wastewater [6].

One of the chemical wastewater treatments is coagulation and flocculation. Coagulation is the process of destabilizing colloidal particles into particles that are easily deposited. Commonly, colloidal particles are difficult to settle because the characteristic of the particles is floating and stable. The coagulation process will increase the clarity of the processing waste because small floating solid particles can be deposited with the help of a coagulant.

Haydar, S. and Aziz, JA [7] conducted coagulation-flocculation research on leather tannery waste using a combination of alum with cationic and anionic polymers. The results showed that the combination of alum with the cationic polymer C-492 resulted in effluent turbidity removal of 97%, total suspended solids (TSS) removal of 93.5%, COD (TCOD) removal of 36.2%, and chromium removal of 98.4%. For this combination, the optimum dose of alum is 100 mg/L as $Al_2(SO_4)_3$ with 5 mg/L C-496. The combination of alum with the appropriate anionic polymer A-100 resulted in effluent turbidity removal of 99.7%, TSS removal of 96.3%, TCOD removal of 48.3%, and chromium removal of 99.7%. Islam, et al [8] researched the efficiency of different coagulants in processing tannery waste in Bangladesh using alum, ferric chloride, and lime, intended as different treatments. After treatment of tannery waste, the pH value was 7.13. The lowest TS is 3833.33 mg/L. Cr^{6+} levels were reduced significantly, as much as 0.07 mg/L. The study recommended a combination of alum and ferric chloride for effective primary treatment of tannery waste.

Coagulation–flocculation is usually practiced using inorganic metal salts such as aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate among which iron salts are generally more efficient than aluminum ones [9]. In recent years polymerized forms of metal coagulants such as polyaluminum chloride (PAC) have been used increasingly for water treatment in Europe, Japan and North America due to reduced cost and wider availability [10], [11]. Such products are claimed to be superior to conventional coagulants because of higher removal of particulate and/or organic matters as well as inherent advantages of lower alkalinity consumption and lesser sludge production [11]. Amokrane and coworkers [9] reported that the percentage removal of COD using conventional coagulants is generally 10–25% with young leachates and 50–65% removal with stabilized leachates or the leachates pretreated by biological means. In this research, the author is interested in using Polyaluminium Chloride (PAC) as a coagulant in the processing of tannery waste. Research was conducted to determine the effectiveness of PAC coagulant in reducing BOD, COD, chromium, TSS, sulfide, and ammonia values in tannery waste processing at the optimum pH and research dose to treat tannary waste.

2. Experimental

2.1. Material

Tannery waste used for this experiment was obtained from a leather factory in Yogyakarta, Indonesia. It also used poly aluminum chloride (PAC) as the coagulant. The characteristic of PAC is white powder with the formula Al(OH)xCly (where x is in the range of1.35–1.65, and y= 3−x). The other materials used were caustic soda (NaOH), sulfuric acid (H_2SO_4), and aquades.

2.2. Determination of Optimum pH

Experiments were conducted using the test jar method. Each experiment was carried out with a beaker glass filled with 300 mL of liquid waste. The PAC mother solution was then added to the waste to obtain 100 ppm PAC. Based on the working pH of PAC at 5-9, pH level variations of 4,5,6,7,8, and 9 were performed in this research. Two variations of stirring were carried out, i.e. fast stirring at 100 rpm for 2 minutes then slow stirring at 25 rpm for 15 minutes.

2.3. Determination of PAC Dosage

Variations of PAC concentration (PAC dosage) were made by adding a mother solution with a PAC concentration of 5000 mg/L into the tannery waste. Five variations of PAC concentration are provided: 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, and 250 mg/L. According to Riva, et al [12], the volume of mother PAC solution added to the waste is calculated using the formula:

$$V1 = (C2 \times V2) / C1$$

where V1 is the volume of PAC mother solution addition, C1 is the concentration of mother PAC solution, C2 is the target PAC concentration, and V2 is the volume of waste processed. The initial pH value was set at the optimum pH of the first experiment. Fast and slow stirring was carried out at 100 rpm for 2 minutes and at 25 rpm for 15 minutes.

2.4. Process Parameters Analysis

To evaluate the performance of PAC as a coagulant in the tannery waste treatment, several parameter analyses were conducted, including turbidity, BOD, COD, TSS, chromium, total nitrogen, total ammonia, total sulfide, and pH. That analysis was carried out based on the method Indonesian National Standards [13], [14], [15], [16], [17], [18] respectively. Analysis was conducted by the Center for Environmental Health Engineering and Disease Control (BBTKLPP) in Yogyakarta, Indonesia.

3. Results and Discussion

Tanning process skin is a stabilizing process skin to withstand attack physics, chemistry, and biology. The tanning process skin done through 4 stages The main processes, namely the beam house operation (BHO), tanning, post-tanning, and finishing processes. The process produces solid and liquid waste. Table 1 is the identification of waste from the tanning industry skin.

Table 1. Identification of Tannery Waste

Stages	Process	Raw Materials	Waste	Waste Characteristics
BHO	Soaking	Water, surfactant	Liquid waste containing residual surfactant Solid Waste : dry blood, feces	Liquid : smelly Solid : smelly
	Liming	Na_2S, $CaCO_3$	H_2S gas, feathers, lime, ammonia	Liquid : soluble, smelly Solid : insoluble Gas: smelly
	Fleshing		Meat residu, fat residu	Solid : smelly
	Splitting		Split skin residu	Smelly
	Deliming	Ammonium sulfat, acid, enzymes	Liquid waste containing ammonia and acid	Soluble, smelly
	Degreasing	Water, surfactant	Liquid waste containing surfactant and natural oil skin	Soluble, smelly
	Pickling	Water, salt, anti-fungal, acid	Liquid waste containing acid, salt and anti- fungal	Soluble, smelly
Tanning	Tanning	Water, $Cr_2(SO_4)_3$, alkali, acid, salt water	Liquid waste containing Cr, Na, and acid	Soluble, hazardous waste, smelly
	Sammying, shaving		Liquid: skin fluid droplets, Solid: skin shaving powder	Liquid: hazardous Solid : hazardous
Post Tanning	Retanning , dyeing, fat liquoring	Neutralizing agent, retanning agent, dyes , oils	Liquid waste containing re-tanning agent, neutralization agent, dyestuff, oil	Soluble, hazardous
	Buffing, trimming		Solid : leather trimming residu	Hazardous

Finishing	Finishing	Pigments , binders	solvent vapor, finisher residue	Gas: smelly Liquid : soluble

Tannery liquid waste contains organic pollutants, metals, dissolved solids, acids, and bases. Waste processing is purposed to reduce the pollutant content in the waste. One chemical waste processing that should be carried out in wastewater treatment processing is coagulation. This process is purposed to obtain particles that are easily deposited. The influence of pH and PAC dose on the effectiveness of PAC coagulation was evaluated in this research by observing process parameters including turbidity, BOD, COD, Chromium, Sulfide, Ammonia, and TSS.

3.1. Determination of Optimum pH

The effectiveness of coagulation process can be seen from the reduction of waste water turbidity. The lower the turbidity value, the clearer the waste resulted from the process.

The influence of pH on the leather waste turbidity values is presented in Figure 1.

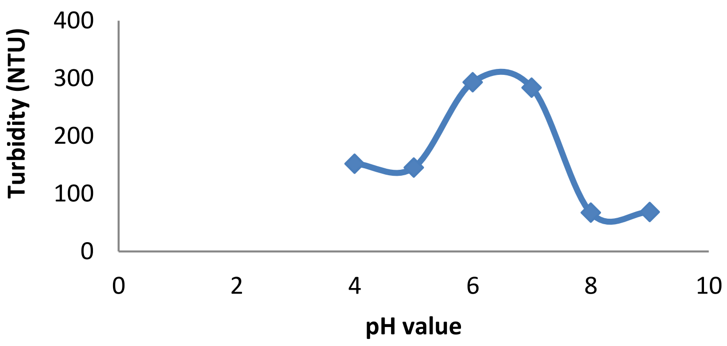

Figure 1. Variation of pH on Turbidity Values

Figure 1 shows that the lowest turbidity occurs at pH 8. This minimum turbidity is then become the basis for determining the optimum pH in waste processing operations using PAC coagulant. From the coagulation process, other parameters might also change. At all pH variations conducted in this study; the BOD, COD, chromium, sulfide, ammonia, TSS, TSS, and pH values were also tested. The results of those parameters observation can be seen in Table 2.

Table 2. Results of BOD, COD, Sulfide, Chromium, Ammonia, pH, TSS Measurements at pH Variations

Variation of pH start	BOD (ppm)	COD (ppm)	Total Chrome (ppm)	TSS (ppm)	Sulfide (ppm)	Ammonia (ppm)	Final pH
Control	635	1842.3	32.4175	346	103.41	72.324	7.7
pH 4	638	1729	4.4165	290	60.59	110.989	3.6
pH 5	630	1504.8	1.9247	333	71.11	118.722	4.9
pH 6	632	1817	1.5782	254	76.89	85.348	6.4
pH 7	630	1567.3	1.968	170	65.22	213.9601	7.3
pH 8	588	1704.8	2.598	68	155.57	312.3321	7.6
pH 9	644	1704.8	2.5068	34	112.34	206.2271	7.8

Based on Table 2, the values of BOD, COD, chrome concentration, and TSS at an optimum pH of 8 decreased from the initial value (control). Meanwhile, sulfide and ammonia increased from the initial value. The pH value of the waste after processing decreased to 7.6. According to Yustinawati, et al [19], the addition of PAC coagulant will affect the pH of the waste. The more coagulant concentration is given, the lower the pH value will be. The use of PAC coagulant causes the release of the hydrogen ions from each hydrogen group produced. The hydrogen ions released increase the hydrogen concentration in the wastewater and decrease the pH value, as can be seen from the following reaction :

$$Al_2(OH)_3Cl_3 \longrightarrow Al_2(OH)_3^{3+} + 3Cl^- + 3H_2O \longrightarrow 2Al(OH)_3 + 3H^+ + 3Cl^-$$

Based on the reaction above, the hydrolysis reaction of PAC releases 3 H^+ ions. The increase of H^+ ions concentration in the wastewater then decrease the pH value, the use of PAC will decrease the pH of wastewater [20]. The optimum pH value of 8 meets the wastewaterquality standards in Indonesia for tannery outlet waste, approximately of pH 6-9.

3.2. Determination of Dosage

Dosage is the amount of substance added per liter or gram of material processed. The PAC dosage variations in this study are 25 ppm, 50 ppm, 75 ppm, 100 ppm, and 125 ppm. The influence of PAC dosage on the tannery waste turbidity is presented in Figure 2.

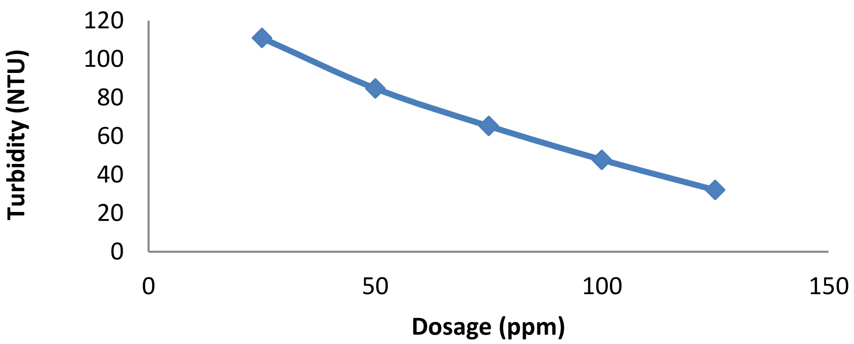

Figure 2. PAC Dosage on Turbidity Value

Figure 2 shows that the lowest turbidity is 32.03 NTU at the highest dose of PAC 125 ppm. The addition of PAC can reduce waste turbidity. The higher the concentration of coagulant added, the more cations are produced. It then increases the floc formation from the colloidal particles bounding and reduces the wastewater turbidity. Along with the coagulation process, several process parameters also change. Table 3 presents the analysis results of BOD, COD, Chromium, Sulfide, Ammonia, TSS, and pH after the coagulation process.

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Table 3. BOD, COD, Chromium, Sulfide, Ammonia, TSS, pH Values at Various Dosage

Dosage (ppm)	BOD (ppm)	COD (ppm)	Sulfide (ppm)	Chrome (ppm)	Ammonia (ppm)	Final pH	TSS (ppm)
Control	635	1842.3	103.41	32.4175	72.324	7.7	346
25	614	1604.8	165.5	3.9935	195.6451	7.6	49
50	514	1779.8	91.3	2.94	144.77	7.6	39
75	634	1579.8	158.35	2.4636	145.991	7.6	25
100	536	1492.3	166.16	1.7948	195.6451	7.6	37
125	429	1617	134.55	1.6649	134.188	7.6	29

Information in Table 3 shows that the lowest BOD, chrome, and TSS values are obtained at a dosage of 125 ppm PAC. Meanwhile, sulfide and ammonia tend to increase. This may be due to the high level of organic pollutants in the waste (as indicated by the BOD and COD values). Part of this BOD and COD may be degraded by microorganisms that produce ammonia and sulfide. Reactions for the decomposition of organic compounds are:

$$CHONSP+O_2+\text{microba-aerobic} \rightarrow \text{new-aerobic-microbes}+H_2O+CO_2+NH_3$$

Based on this reaction, as long as there are organic pollutants in the waste, decomposition will occur by microbes with the presence of oxygen and produce new ammonia and hydrogen sulfide.

3.3. *Effectiveness of PAC in reducing BOD, COD, chromium, TSS, sulfide, ammonia*

The effectiveness of PAC in reducing the BOD, COD, chromium, and TSS was also studied. Figure 3 shows the % reduction of BOD and COD at various dosages of PAC

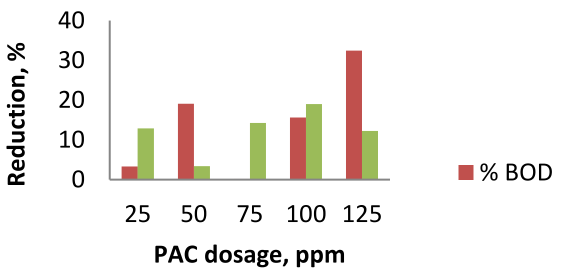

Figure 3. %Reduction in BOD and COD at PAC dosage

In processing leather waste with 125 ppm PAC coagulant, a reduction in BOD of 32.44% and COD of 12.22 % was obtained. These results indicate that coagulation using PAC can reduce easily decomposed organic compound pollutants higher than total organic compounds. The BOD value shows the number of organic compound pollutants that are easily decomposed, while COD shows the total number of organic compounds that are both easily decomposed and those that are difficult to decompose. PAC is a coagulant that functions to precipitate colloidal particle pollutants in waste. Colloidal particles are particles similar to milk, which if they are deposited using normal physics cannot settle quickly. So these colloidal particles are more effectively deposited using chemical methods, one of which is coagulation-flocculation. Organic pollutants can be in the form of colloidal particles or suspensions and solutions. Colloidal organic pollutants can be processed by coagulation, and other organic particles can be processed by other processes. Organic pollutants can also be processed further by biological processing with the addition of aerobic and anaerobic bacteria. So in further research the effectiveness of biological processing can be tested on reducing BOD and COD values.

In this study, the % effectiveness of PAC coagulant in reducing chrome levels was also measured, which can be seen in Figure 4.

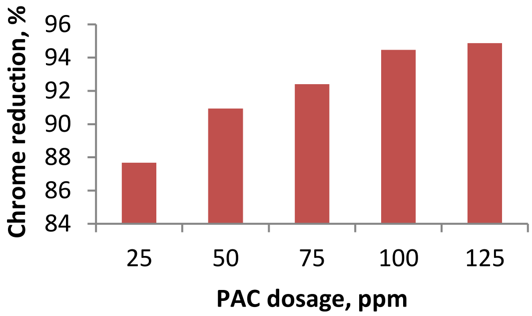

Figure 4. %Reduction of Chromium at Various PAC Dosage

In Figure 4, a high reduction of chrome levels was obtained, reaching 94.26 % at a PAC dosage of 125 ppm. Chrome at pH 5 has precipitated to form chrome hydroxide. In the PAC coagulation process at a dosage of 125 ppm, the reduction of chromium was relatively high. Setting the initial pH to 8 and adding PAC was able to precipitate chrome well. However, this result does not meet the BMAL for leather waste, as much as 0.6 ppm. At a PAC dosage of 125 ppm, the final chromium content was obtained at 1.66 ppm. These results indicate that further processing is necessary to reduce the amount of chrome in the outlet waste.

The percent reduction in TSS was also measured at various PAC dosages of 25 ppm, 50 ppm, 75 ppm, 100 ppm, and 125 ppm, as presented in Figure 5.

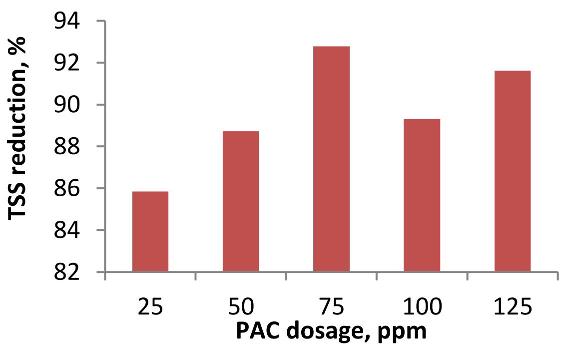

Figure 5. %Decrease in TSS with Varying PAC Dosage

Figure 5 shows that the TSS reduction reached 91% at a dose of 125 ppm. TSS is the total solid suspension, i.e. the solids retained on the 2.0 µm paper filter. This TSS can include colloids or suspensions (coarse solids). The greater the concentration of coagulant added, the more cations are produced from the coagulant, and the more colloidal particles in the waste are neutralized and form floc. When excessive coagulant concentration is added, the TSS value will increase, this occurs due to the process of excessive absorption of cations by colloidal particles in the waste, causing deflocculation or colloid restabilization.

4. Conclusion

The optimum pH value for processing tannery waste with PAC coagulant is 8. The highest turbidity reduction was obtained at a PAC dosage of 125 ppm. At this dosage of 125 ppm, the BOD reduction is 32.44%, COD reduction is 12.23%, chromium reduction is 94.86%, and TSS reduction is 91.62%. PAC coagulant with a dose of 125 ppm in tannery waste increases the sulfide value from 103 ppm to 134 ppm and ammonia from 72 ppm to 134.11 ppm due to organic compounds decomposition.

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6. Conflicts of interest

There are no conflicts to declare

7. Formatting of funding sources

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