The Effectiveness of Poly Alumunium Chloride (PAC) on Chemical Oxygen Demand (COD) Levels of Laundry Wastewater in Batam City, Indonesia

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The Effectiveness of Poly Alumunium Chloride (PAC) on Chemical Oxygen Demand (COD) Levels of Laundry Wastewater in Batam City, Indonesia

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Abstract**—** *Laundry activities produces waste water contains high pollutants such as Chemical Oxygen Demand (COD). The COD level of sample from a laundry wastewater was 541 mg/L, which over the wastewater quality standard the Indonesian Minister of Environment Regulation no 5/2014 (100 mg/L), therefore wastewater treatment was required to prevent any adverse effect. One of the parameters which is able to describe the pollutants in wastewater is COD. Wastewater treatment can be done by coagulation-flocculation process with Poly Aluminum Chloride (PAC) coagulant. The purpose of this study was to determine the efficiency of PAC in reducing COD levels in laundry wastewater. This study was a true experimental study with a pre-test post-test with control group design, used jar test to simulate the coagulation-flocculation process in a laboratory scale. PAC variations concentration were 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L with additional samples of pretest and control. The treatments were repeated in 6 times. Kruskal Wallis test showed population of COD level difference before and after treatment (p=0.008). Mann Whitney test showed that groups which had significant difference in COD reduction were between the control group and each of PAC-treated group (p<0.05). The optimum concentration of PAC in reducing COD levels was 300 mg/L with an average effectiveness of 58.97%. The final COD levels in this study still requires further wastewater treatment before the final disposal.*

Keywords**— *Chemical Oxygen Demand (COD), Laundry, Wastewater, Poly Aluminum Chloride (PAC).***

I. INTRODUCTION

The laundry activities were widely used by the community to help with household activities, along with the increasing demands in the communities. The development of a laundry activities must be equipped by waste management before wastewater diposal to water bodies.(Wicheisa et al., 2018; Yusmidiarti, 2018) Laundry wastewater has high pollutant levels, which can be seen from chemical parameters such as Biological oxygen demand (BOD), chemical oxygen demand (COD), phosphate, physical parameters such as total suspended solid (TSS), and total dissolved solid (TDS) (Pratiwi et al., 2012). The results of COD measurements carried out on laundry wastewater X showed a COD level of 541 mg/L and there was a wastewater treatment process. This figure exceeds the quality standard of the Indonesian Minister of Environment Regulation Number 5 year of 2014 concerning Wastewater Quality Standards, which is 100 mg/L for group I wastewater (Menteri Negara Lingkungan Hidup, 2014)

Chemical substances derived from detergents contain complex chemical compounds including surfactants, builders, bleaches, and additives (Apriyani & Nani, 2017) These substances can increase the COD level of wastewater. COD is defined as the equivalent amount of oxygen used in the chemical oxidation of organic matter. COD measurements were measured using strong oxidants to oxidize organic matter which would only be partially oxidized by microorganisms. Organic and inorganic components can be oxidized during COD measurement.(Hu & Grasso, 2004)

Wastewater with high levels of COD if discharged into the environment without going through several treatment will exceed the water's ability to adjust with the conditions in the water, so that bacteria grow rapidly and consume dissolved oxygen which causes a decrease in dissolved oxygen levels. Organisms in water such as protozoa and fish will find it difficult to live without dissolved oxygen.(Aini et al., 2017) Laundry waste also contains phosphate which can cause eutrophication, because phosphate is a nutrient for algae. Leftover detergents also contain toxic compounds that can be harmful to life in the water and to humans who use the water.(Yusmidiarti, 2018)

Poly aluminum chloride (PAC) is one of the coagulants commonly used in the coagulation and flocculation processes of wastewater treatment because it is safe and economical. PAC is a collection of complex inorganic compounds, hydroxyl ions, and aluminum ions with different degrees of chlorination that form polynuclear. The general formula for PAC is $Al_m(OH)_nCl_{(3m-n)}$. PAC can reduce COD levels up to 62%-83% in a study conducted by Yustinawati in 2014 with oil well drilling waste (Yustinawati, 2014). Some of the advantages of PAC are it can coagulate water with different turbidity in a short time, produces less sludge, and only leaves a small amount of aluminum residue in the water. Another advantage of PAC is that it can work in a wide pH range, strong adsorption rate, and high floc formation rate even though the dose given is small.(Murwanto, 2018; Rahimah et al., 2016) This study aims to determine PAC effectiveness in decreasing COD levels in laundry wastewater X.

II. METHOD

This research was using true experiment, pretest post-test with control group design. The sample used was wastewater produced by laundry X which located in Batam City, Indonesia. Samples were taken by grab sampling for 6 times repetition in different days. The total samples taken were 36 samples consisting of 4 treatment samples, 1 control sample, 1 pretest sample, and repeated 6 times. The pretest sample was first measured for temperature, pH, and COD levels and used as data before treatment. The measurement results of temperature, pH, and COD levels of control and treatment groups were used as data after treatment (post test).

The independent variables used were variations in PAC concentration of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L. Dosing of PAC was done by making a 1% PAC solution and calculating the volume of the PAC solution needed to reach 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L concentration according to the dilution formula, then adding it to 500 mL of the wastewater sample. The control sample was not treated with PAC coagulant, but the stirring process was still conducted. The dependent variable was the COD level of laundry wastewater X which will be proceeded by calculating the reduction in COD levels and the efficiency of the reduction. There were confounding variables in this study. The pH value and temperature were confounding variables measured, while the confounding variables which controlled were mixing speed, mixing time, and processing capacity.

Samples were stirred using a jar test. The stirring speed for rapid mixing was 100 rpm with a stirring time of 1 minute, followed by slow mixing of 40 rpm with a stirring time of 20 minutes. Precipitation was done for 1 hour. Then the samples were examined for COD levels using the open reflux method based on APHA-5220-B standard.(Rodger B. Baird, Andrew D. Eaton, 2018)

Calculation of COD reduction efficiency using the formula:

$$\% \text{ Efficiency} = \frac{\text{COD level pretest} - \text{COD level post test}}{\text{COD level pretest}} \text{ X } 100\%$$

Data analysis of the difference in COD levels before and after various treatments was carried out using the Saphiro Wilk normality test, followed by a homogeneity test as a fulfillment of assumptions. The Kruskal Wallis test was conducted with the hypothesis that there were differences in the decrease in COD levels in each group, and the Mann Whitney follow-up test was used to determine the pairs of groups with significant and non-significant differences.

III. RESULTS AND DISCUSSION

Laundry X served 5-30 customers every day. In one time wash, 30-100 mL of liquid detergent was used, and 50-100L of water was used. In one time wash, the amount of dirty laundry could reach 5 kg.

The results of testing the COD levels of the laundry wastewater pretest sample X for 6 days had an average of 442.83 mg/L (see Table 1.). This figure exceeds the quality standard of the Minister of Environment Regulation Number 5 of 2014 for group I wastewater, which is 100 mg/L for COD. Fluctuating COD levels were influenced by the amount of detergent used, water usage, and the presence of impurities in the laundry. The results of the pH value of the pretest group tended to be neutral and still met the quality standard of 6-9, except for the 1st and 6th repetitions which did not qualify the quality standard (see Table 3.). In this study, no pH adjustment was made with the consideration that PAC can work in a wide pH range. The average temperature for pretest samples were 26,88ºC, with the minimum temperature of 25,9ºC dan maximum temperature of 27,9ºC (see Table 4). The temperature measurement for 6 times repetition was considered normal and still meets the 38ºC temperature quality standard treshold according to Regulation of the Minister of Environment 5/2014.

A. Chemical Oxygen Demand (COD)

After the rapid mixing process and slow mixing, the floc formed was precipitated for 1 hour, so that the floc gathered at the bottom of the beaker glass due to gravity. The floc formed was less than 1 mm in size. The formation of flocs in the samples treated with PAC coagulant can be occurred after the wastewater was stirred.

Flocs were formed as a result of PAC mixed in. There was a destabilization of colloids and suspended particles through neutralization of electric charges so that the force of repulsion of similar electric charges between particles was reduced. PAC had a high positive electric charge, as well as a long polymer chain so that it easily increased the covalent attraction between particles.(Firra & Mohamad, 2013) The electrolyte that played a role in this coagulation process is Al^{3+} cation. In the study, laundry wastewater which was originally turbid and colored, after the addition of PAC coagulant became clear, because the positive ions Al^{3+} bind organic ions that were negatively charged in the wastewater.(Susanti & Hartati, 2003)

The average post-test COD levels in the control group, with variations in the treatment doses of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L, respectively, were 397.83 mg/L, 172.50 mg. /L, 181.50 mg/L, 194.83 mg/L, and 220.67 mg/L. This showed that in laundry wastewater X after being given a variety of treatments, the COD level has decreased. However, the average COD content of all groups still exceeded the specified quality standard stated in Regulation of the Minister of Environment 5/2014 which is 100 mg/L.

Table 1. COD Level Measurement Results

Repetition	pretest (mg/L)	Post test (mg/L)				
		Control	300 mg/L	350 mg/L	400 mg/L	450 mg/L
1	541	559	263	311	289	400
2	337	407	187	192	184	198
3	483	372	88	133	156	220
4	584	445	129	165	152	139
5	348	262	137	108	209	174
6	364	342	231	180	179	193
Average	442.83	397.83	172.50	181.50	194.83	220.67

In the control group, COD was increase, it could be seen in the 1st and 2nd repetitions that the COD post-test levels in the control group increased. This can be due to changes in temperature that occur. Temperature affects the physical, chemical, and biological properties of wastewater. Changes in temperature cause an increase in viscosity, evaporation, and volatilization. As a result, the structure of the colloidal particles became smaller. This caused the ability for deposition to decrease. In the control group, only mixing and precipitation was done. The increase in COD was due to the fact that the colloidal particles cannot be deposited, so that when measuring COD levels, organic matter was carried in the sample. This was in line with Ayu Larasati's 2017 research in the study of decreasing COD levels of laundry wastewater using $FeCl_3$ coagulant which study showed that the control group in the 2nd and 3rd repetitions experienced an increase in COD levels from an initial level of 1.012 mg/L to 1,680 mg/L, and from an initial level of 717 mg/L to 979 mg/L.(Larasati et al., 2017)

The mixing process with the jar test in the control group without PAC treatment can also reduce COD levels because the stirring process could increase the dissolved oxygen content in the water. With the availability of oxygen in the water, the need for oxygen decreased, so that the COD level decreased. A similar thing happened in Islamawati's 2018 study which showed that the COD level of control group in the study of decreasing COD levels of tapioca wastewater that was treated with jar test mixing was indeed decreasing.(Islamawati et al., 2018)

Table 2. COD Levels Reduction

Group	COD levels average (mg/L)		Difference (mg/L)	Efficiency (%)
	Pretest	Post test		
300 mg/L	442.83	172.50	270.33	58.79
350 mg/L	442.83	181.50	261.33	58.21
400 mg/L	442.83	194.83	248.00	54.07
450 mg/L	442.83	220.67	222.17	49.16

The decrease in COD levels in the treatment group showed in Table 2 was due to the negative ionized organic matter already bound with the positive ions from the PAC coagulant and forming flocs. The flocs settle to the bottom of the beaker glass due to gravity and were separated from water which has a lower density and clearer color. The clearer water has lower COD levels due to the process of removing organic matter. This was corresponding with the 2018 study by Ulima where PAC in slaughterhouse wastewater samples can cause COD levels to decrease by up to 40%.(Salsabila et al., 2018)

B. pH value

The results of pH value in the pretest and posttest treatment samples in 6 times repetition were as follows:

Table 3. pH Measurement Results

Repetition	Pretest	Post test				
		Control	300 mg/L	350 mg/L	400 mg/L	450 mg/L
1	5.98	5.8	4.61	4.55	4.5	4.48
2	6.53	6.6	4.4	4.4	4.39	4.38
3	6.97	6.86	4.31	4.33	4.33	4.37
4	6.96	6.98	4.6	4.56	4.53	4.51
5	6.69	6.8	4.44	4.42	4.42	4.41
6	9.95	10.08	8.95	8.69	8.4	8.04

The results of measuring pH value before and after treatment with 6 times repetition for the control group, variations in the treatment doses of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L in the table show that PAC can cause a decrease in pH. The more PAC given, the more acidic the pH of the wastewater. This was in line with Yustinawati's research in 2014 where the pH level of the drilling mud waste after being treated with PAC decreased by ±2 from the initial pH.(Yustinawati, 2014) Husaini's 2018 research also showed that PAC could lower the pH level in gold processing wastewater.(Husaini et al., 2018)

The decrease in pH was caused by the addition of PAC. H^+ ions were released into the water for each hydrogen group produced. The PAC reaction in water can be described as follows: $Al_2(OH)_3Cl_3 \rightarrow Al_2(OH)_3^{3+} + 3Cl^- + 3H_2O \rightarrow 2Al(OH)_3 + 3H^+ + 3Cl^-$. Product of $3H^+$ ions causes pH level to decrease became more acidic.(Yustinawati, 2014) This can affect the next wastewater treatment, thus neutralization is required.

C. Temperature Measurement

The results of temperature measurements on the pretest and post test samples of treatment in 6 times repetition were as follows:

Table 4. Temperature Measurement Results

Repetition	Pretest (ºC)	Post test (ºC)				
		Control	300 mg/L	350 mg/L	400 mg/L	450 mg/L
1	26.4	25.5	25.5	25.3	25.3	25.2
2	27.4	26.7	26.6	26.4	26.5	26.5
3	27.2	25.5	25.2	25.2	25.1	25.2
4	26.5	24.3	24.5	24.6	24.4	24.4
5	25.9	24.6	24.5	24.4	24.4	24.3
6	27.9	27.9	27.6	27.3	27.1	27.2

The results of the measurement of the temperature of the wastewater sample can be seen in the table above. The temperature of the treatment group decreased from the results of the temperature measurement of the pretest group with a difference of ±1ºC. All temperatures of the group qualify the quality standard according to Regulation of the Minister of Environment 5/2014 which was 38ºC because they were still adjusting to room temperature.

D. COD Reduction Efficiency

The following was a graph of the efficiency of reducing COD levels in the control group and various doses of PAC treatment:

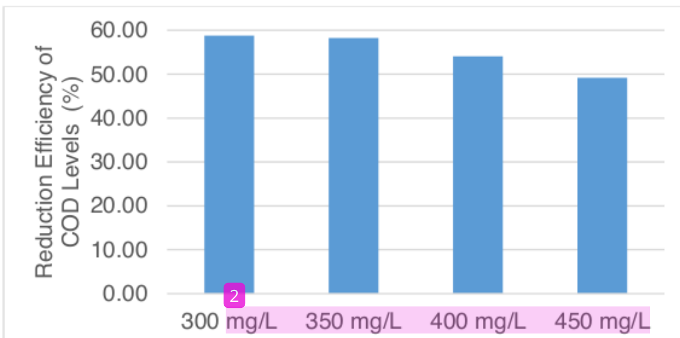

Fig. 1 COD level Reduction Efficiency

According to the COD levels in the pretest and posttest groups in Table 2, there was a decrease in COD levels. The average decrease in COD levels for the group with PAC doses variation of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L were 270.33 mg/L, 261.33 mg/L, 248 mg/L, and 222.17 mg/L. The COD reduction efficiency in the four groups were 58.79%, 58.21%, 54.07%, and 49.16%, respectively. From these results, it can be concluded that laundry X wastewater treated with PAC coagulant causes a decrease in the level of COD parameters.

Treatments with doses of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L showed lower efficiency and lower COD levels decrease at higher dose. This was caused by colloid re stabilization that occurs when high doses of coagulant were given to wastewater, there was excessive absorption of cations by colloidal particles. So that the positive ions of the coagulant were no longer able to adsorb the negative ions of colloidal particles. This also caused the wastewater that was given a dose of coagulant that has passed the optimum dose to increase turbidity.(Susanti & Hartati, 2003; Yustinawati, 2014) So that the decrease in COD levels was more significant at lower dose of coagulant. The PAC dose of 300 mg/L was the optimum dose for this study.

Similar result occurred in Adysti's research in 2014 for treating laundry wastewater using combination wastewater treatment using PAC and active carbon filtration. In the research, the optimum dose was 55 mL/L, whereas the higher doses showed the decreasing efficiency of COD removal.(Maretha N et al., 2014)

COD levels reduction data before and after treatment did not meet the normality assumption. One of the data category, which was group of 450 mg/L PAC variation was not distributed normally. Meanwhile homogeneity assumption terted with Levene test shown that the COD levels reduction data were homogen. Further test conducted with non parametric tests.

Based on a test using the Kruskal Wallis test, it was concluded that there were differences in the pretest and posttest COD levels in the control group, and the treatment group with variations in PAC doses of 300 mg/L, 350 mg/L, 400 mg/L and 450 mg/L with a significance 0.008 (significance <0.05, H0 rejected). Thus, further tests were conducted with the Mann Whitney test. The results showed that the groups that had significant differences were between the control group and the PAC dose of 300 mg/L, the control group and the PAC dose group of 350 mg/L, the control group and the PAC dose group of 400 mg/L, and the control group and the PAC 450 mg/L dose group. Meanwhile, between each of the groups of treatment dose variations, there was no significant difference.

The ability of PAC in reducing COD levels of laundry wastewater X was still not optimal, because post-treatment COD levels still exceeded the quality standards set by Ministerial Regulation Number 5 year of 2014. Therefore, further wastewater treatment is required to result laundry wastewater with COD levels that qualify the requirements for discharge into water bodies.

IV. CONCLUSION AND RECOMMENDATIONS

The average efficiency of COD levels reduction in the treatment group of PAC coagulant doses of 300 mg/L, 350 mg/L, 400 mg/L, and 450 mg/L respectively were 58.79%, 58.21 %, 54.07%, and 49.16%. The optimum dose of PAC in this study was a dose of 300 mg/L with an average effectiveness of 58.79%.

The test using the Kruskal Wallis test on the decrease in COD levels of laundry wastewater X showed a significance of 0.008 (significance <0.05, H1 was accepted), so it was concluded that there were differences in the decrease in COD levels of laundry wastewater X between groups. Mann Whitney follow-up test showed that the groups that had significant differences were the control group with each every one of treatment dose variation.

The COD level of laundry wastewater after treatment with various doses of PAC coagulant still exceeded the wastewater quality standard stipulated by the Minister of Environment Regulation No. 5 year of 2014. Further treatment is required so that the quality of wastewater is feasible to be discharged into water bodies.

Suggestions for future researchers is to expand the range of pollutant parameters tested for laundry wastewater such as phosphates, detergents, and others. The next research may conduct pH control to optimize the ability of the coagulant used and the next research also may do a combination of wastewater treatment with biological treatment so that the final pollutant parameter qualified the referenced quality standard.

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PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7