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Application of sodium hypochlorite (NaOCl) for ammonia removal in wastewater effluent of PT. HS

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Abstract. PT HS is the world's leading toy manufacturing company with more than 6,000 workers. Due to the high number of workers in PT. HS, it will impact to domestic activities (toilet discharge). Based on the annual report for wastewater effluent, ammonia from PT HS's wastewater effluent exceeded the standard parameter from Jababeka Industrial Estate with most cases reaching 50 mg/L. Whereas, the Jababeka Industrial Estate regulation states that the maximum ammonia allowed in wastewater effluent is 10 mg/L. **Objectives:** The objectives of this experiment are to know the optimum dose of NaOCl 9% on ammonia removal and to know the concentration of residual chlorine after the treatment process. **Method and results**: This research the experimental laboratory method to get the primary data which uses the artificial sample as waste water sample based on SNI guideline. The results showed that exposure to sodium hypochlorite reduced ammonia concentration in wastewater samples from 50 mg/L to 8.9 mg/L. The ammonia decreased by adding 110 mg/L of NaOCl 9% solution within 30 minutes of contact time and resulting the residual chlorine 0.72 mg/L. The residual chlorine was still in the standard limit did not exceed mg/L. The results also showed that the dose variations of sodium hypochlorite influence ammonia removal. Also, mostly the total residual chlorine forecast will increase with the increasing sodium chlorine dose. **Conclusion:** The chlorination process was effective to reduce the ammonia concentration. Also, the residual chlorine was still in the standard limit which not exceed from 1 mg/L. The result also shows that the dose variations of sodium hypochlorite influence ammonia removal efficiencies.

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1 Introduction

The fast rapid industrial development today is not only bring a positive impact on the economic growth in Indonesia, but also has a negative impact on environmental qualities. And one of the example that can give the negative impact to environment is wastewater which produce by domestic actvities [1]. Hence, the improvement should be needed from related parties which can be from the government through standardization and regulation about environmental management. This standarization and regulation aim to reduce the negative impact on the environment resulted by the industry [2].

One of the manufacturing industry which produce a wastewater is PT HS. It is a world's leading toy manufacturing company with more than 6,000 workers. Due to the high number of workers in PT. HS, it will impact to domestic activities (toilet discharge) with the flow rate 343 m^3/day of wastewater effluent. Therefore, PT. HS should be paid more attention to wastewater discharge that might be impact to the environment. Besides that, because PT. HS is located in Jababeka industrial estate that has the estate regulation for the wastewater discharge. Therefore, the PT. HS should be comply on that regulation. In the industrial estate regulation contains several standard parameter by the color, turbidity, total coliform, nitrite and nitrate, ammonia, etc [3]. The standard effluent for wastewater discharge based on Jababeka estate regulation is shown in Table 1.

Table 1. Estate regulation of Jababeka Industrial area, 2012.

NO	PARAMETER	QUALITY STANDARD	UNIT
	PHYSICAL		
1	Temperature	40	^oC
2	Dissolved solid	2.000	mg/L
3	Suspended Solid	400	mg/L
4	Color	200	PtCO
	CHEMICAL		
5	BOD (Biochemical Oxygen Demand)	500	mg/L

6	COD (Chemical Oxygen Demand)	800	mg/L
7	pH	6 – 9	-
8	Ammonia Total (NH3)	10	mg/L
9	Detergent	5	mg/L
10	Phenol	0.5	mg/L
11	Vegetable Oil	5	mg/L
12	Mineral Oil	15	mg/L
13	Nitrate (NO3)	30	mg/L
14	Nitrite (NO2)	2	mg/L
15	Sulfite (H2S)	0.1	mg/L
16	Arsenic (As)	0.1	mg/L
17	Barium (Ba)	2	mg/L
19	Cadmium (Cd)	0.05	mg/L
20	Chromium total (Cr)	0.5	mg/L
21	Chromium hexavelent (Cr VI)	0.1	mg/L
22	Cobalt (Co)	0.4	mg/L
23	Copper (Cu)	2	mg/L
24	Cyanide (CN)	0.05	mg/L
25	Fluoride (F)	2	mg/L
26	Iron (Fe)	5	mg/L
27	Lead (Pb)	0.1	mg/L
28	Manganese (Mn)	2	mg/L
29	Mercury (Hg)	0.002	mg/L
30	Nickel (Ni)	0.2	mg/L
31	Zinc (Zn)	5	mg/L
32	Stannum (Sn)	2	mg/L
33	Selenium (Se)	0.05	mg/L

On the other hand, according to waste water sampling report Jababeka (Doc. No. 6916/LHU/LAB-JI/VIII/19), noted that parameter ammonia from PT HS's wastewater effluent was exceeding the industrial estate limit and the ammonia concentration test results can be seen in (graphic 2). Ammonia in surface water comes from urine and feces, also from microbiological oxidation of organic substances (HaObCcNd) that usually from natural water or industrial and residential wastewater. Ammonia is a colorless gas or liquid that has a different odor. In a dissolved, ammonia comes in two forms. One of which is ammonia toxic gas and ammonia ion which is less toxic NH_4^+. The composition depends on the amount of pH and temperature of the wastewater [4]. Ammonia levels in effluent wastewater must be minimized because it can be harmful to the ecosystem in the water and not only that, ammonia will also be oxidized by microorganisms through a nitrification process that will convert nitrites into nitrates so that they can endanger humans. Wastes with high levels of ammonia can also be produced from domestic processes and production processes [5].

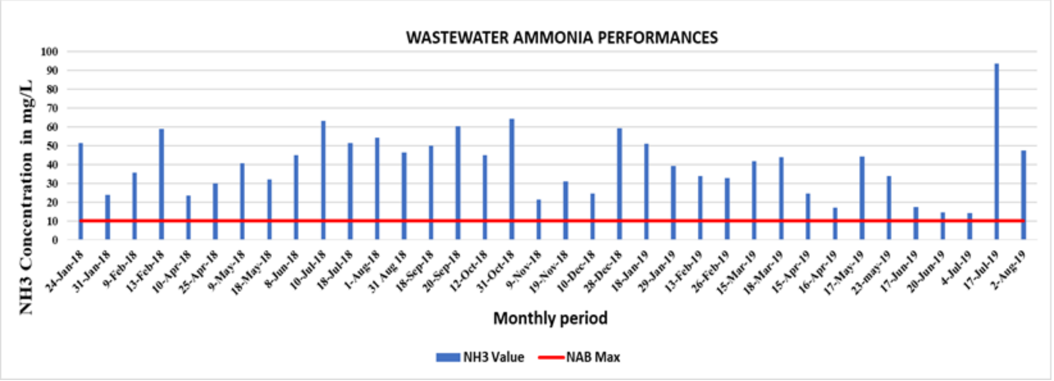

Fig 1. Monthly report of PT HS for ammonia concentration in wastewater effluent (mg/L) *(source: PT. HS monthly report)*.

Based on the annual data which can be seen in Fig. 2, the average ammonia is exceed around 50 mg/L. But, the standard parameter based on Estate Regulation Jababeka is 10 mg/L. Hence, the company must pay the extra charging due the consequent of the exceeding parameter. The extra charging that PT. HS has been pay is shown below:

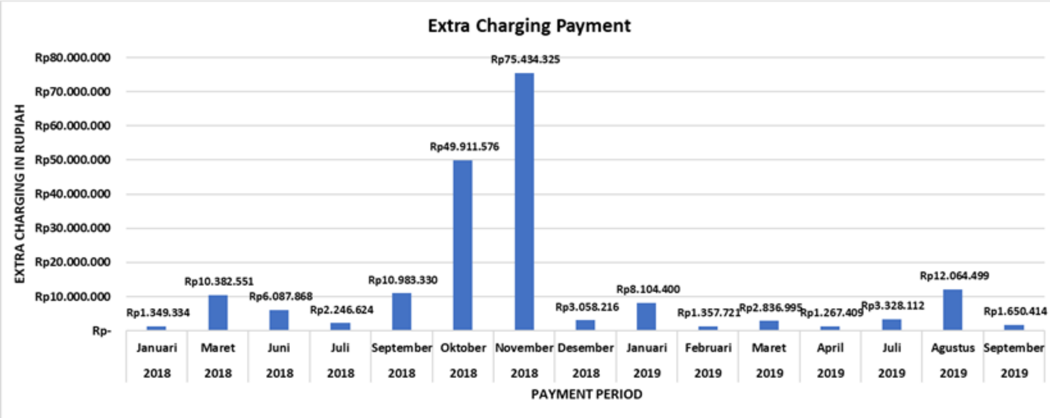

Fig 2. Monthly report of extra charging for ammonia concentration that exceed from the standard (Rupiah) *(source: PT. HS monthly report)*.

Thus, it is necessary to treat wastewater first before being discharged into the environment through several methods of treating wastewater both biologically and chemically. Separation process is carried out to separate ammonia from wastewater generated from a production process and domestic. This separation process can remove ammonia by several methods such as ammonia water stripping, ion exchange, biological nitrification-denitrification, or chlorination [6]. The application of the ammonia separation process in wastewater depends on several factors, namely the level of contamination, the acidity of the pH and others. Hence, this research will use chlorination as a method to reduce ammonia content in wastewater. Where in the chlorination process occurs a reaction between chlorine with ammonia which can produce chloramines. Then, if chlorine continues added until there is free residual chlorine, it will used as addition to chlorine combined in mono, di, or form tri-chloramines. In the ammonia chlorination reaction, nitrogen tri-chloride is the last step before reaching the point of optimum chlorination. In practice nitrogen tri-chloride is always found along with a small amount of the chlorination [7]. The reason why use chlorination method for amonia removel is because 80-95% effectively can remove ammonium, not sensitive to toxic substances and temperature, adaptable to existing facilities [8, 9]. In this method, chlorination can usually use the water as chlorine gas (Cl_2), sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$) or chloroamine (NH_2OCl). Furthermore, this research choose sodium hypochlorite as ammonia removal because easy to use and and handle [10]. Hence, this paper will discuss the effectiveness doses of using sodium hypochlorite as a chlorination process to reduce ammonia content in wastewater and to know the residual chlorine concentration after the treatment. This paper also has a limitation study that the ammonia concentration is artificial sample and if apply in the real, the doses it will range enough.

2 Method

This research was conducted at a laboratory scale using artificial samples which containt of 50 mg/L (mg/L) ammonia refer to the SNI 01-3554-2006 guideline as the reference for residual chlorine test in wastewater using N,N Diethyl-1,4 Phenylenediamine Sulfate (DPD) as the reagent and spectrophotometry as a tool. An artificial sample was an object of research which composition was made in such a way as an approach in real sample.

2.1 Artificial Sample Preparation

This stage includes the process of making artificial water samples as research objects. Artificial samples that refer to the method of making standard solutions in accordance with SNI 06-6989.30-2005. Making artificial samples begins with dissolving ammonium chloride as much as 0.3819 grams in 100 mL aquadest which will be the ammonia standard solution of 1000 mg/L. Then, make an artificial sample containing 50 mg/L of ammonia by piping 50 ml from the ammonia standard solution and adding distilled water to the mark of 1 liter.

2.2 Variables of the Experiments

The control variable of the experiments was the total ammonia concentration which was 50 mg/L. Furthermore, an independent variables were designed is sodium hypochlorite (NaOCl) dose variations. The dependent variable was the decreasing amounts of total ammonia concentration that represents the removal efficiency of sodium hypochlorite. The concentration of sodium hypochlorite solution is 9% of Chlorine.

2.2.1 Sodium Hypochlorite Trial Dose Variations

In this experiment use sodium hypochlorite with 9% purity. The variation of NaOCl doses consist of 8 doses which shown below:

Table 2. NaOCl 9% dose variations

NO	Volume of NOCl 9% (mL)	NOCl concentration(mg/L)
1	0,018	20
2	0,027	30
3	0,5	55
4	1	110
5	1,5	165
6	2	220
7	0,33	300
8	0,39	350

Then, those all doses (see Table 2) are adding to 1 liter water sample that contain of 50 mg/L ammonia concentration, the treatment process conducted in closed beaker glass to make the treatment more oxidize perfectly and stirred with magnetic stirrer 100 rpm [11] for 30 minutes contact time [12]. This treatment was conducted twice every dose variations (by duplo treatment).

2.3 Determination of ammonia levels

This research was used the SNI 06-6989.30-2005 guideline to test the ammonia concentration in wastewater which use spectrophotometry as a tool. The steps of the ammonia test is shown in figure below:

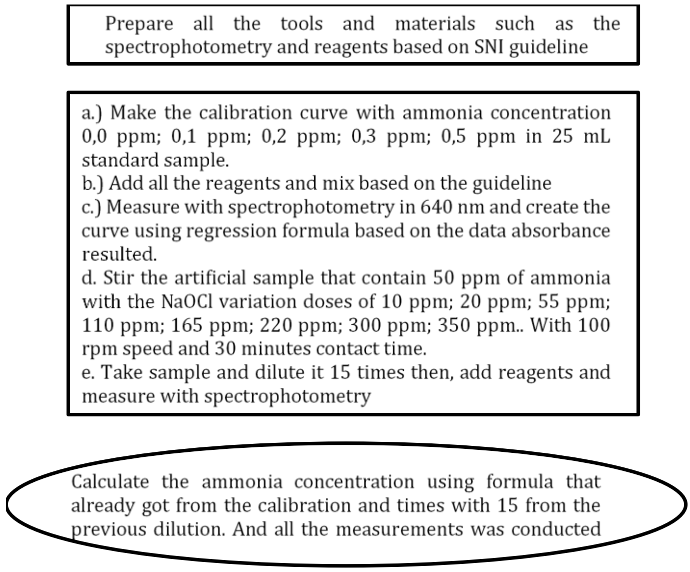

Fig 4. The steps of the ammonia concentration test based on SNI guideline *(source: SNI Guideline in 2005)*.

2.4 Determination of chlorine concentration

This research is use the SNI Guideline as the reference for residual chlorine test in wastewater using DPD spectrophotometry as a tool and DPD powder pillow as the reagent. The steps of the chlorine residual test is shown in figure below:

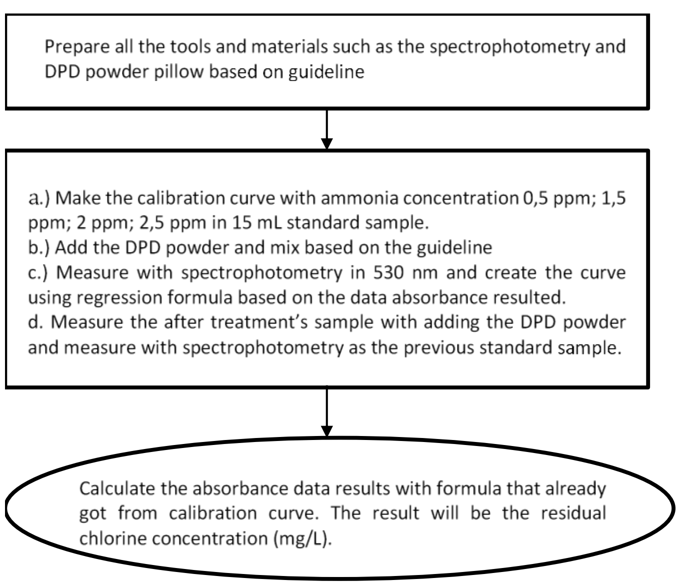

Fig 5. The steps of the residual chlorine concentration test based on SNI guideline *(source: SNI Guideline in 2006)*.

3 Results and Discussion

3.1 Data Collection and Analysis

With 50 mg/L of initial ammonia concentration and stirred within 30 minutes with magnetic stirrer, the water sample directly measured to know the ammonia concentration and residual chlorine concentration. After conducted the measurement using SNI guideline in the laboratory, it is obtained results on the following table 3 below:

Table 3. Ammonia concentration after treatment using NaOCl 9%

NO	DOSE (mL)	Dose (mg/L)	Concentration ammonia after treatment	Decrease level in percentage
1	0,05	55,5	14,0	72%
2	0,1	111	8,9	82,2%
3	0,15	166,5	13,3	73,4%
4	0,2	249,75	11,8	76,4%

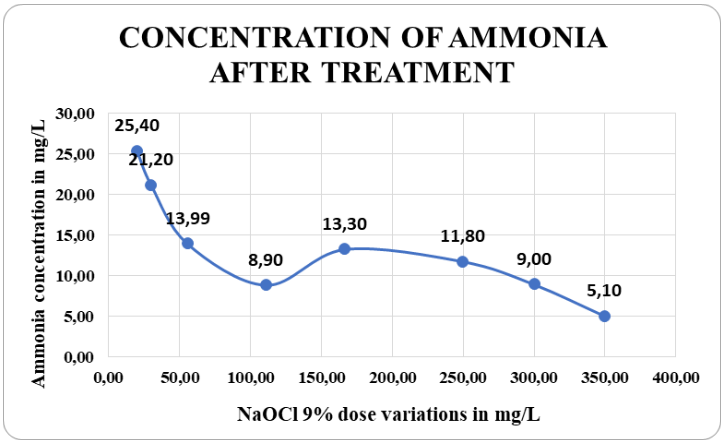

Fig 6. Graphic plot for ammonia concentration after treatment *(source: data calculation).*

After got the ammonia concentration after the treatment process, we also must test the chlorine residual as the base requirement to keep the good sewerage quality. The data for chlorine residual after the test is shown in the Fig 7 below:

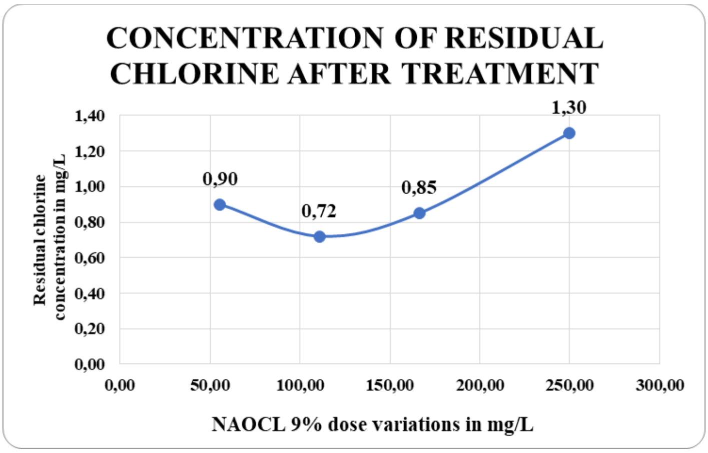

Fig 7. Graphic plot for residual chlorine concentration after treatment *(source: data calculation).*

As we can see from those graphic above, the optimum point was happened when the NaOCl 9% with 110 mg/L dose was added in sample that contain of 50 mg/L ammonia concentration, it will reduce until 8,9 mg/L ammonia concentration and the residual chlor was 0,72 mg/L which will not danger for the sewerage in PT HS because, it's still less than 1 mg/L [13]. If the residual chlorine is high, it can dilute with water to reduce the residual chlorine. According to the reference, the optimum point happens when the N_2 gas is form and there will be happen of reaction process as following below:

$$2NH_2Cl + HOCl \rightleftharpoons N_2 + 3HCl + H_2O$$

At a dose of 110 mg/L after passing the optimum point, the chlorine continues added will be free chlorine which is as disinfectant [14]. Then, it can be explained further that the optimum point formed because, the continued addition of chlorine causes chlorine it reacts with ammonia to form chlorine. If added chlorine continued, the chlorine will react with chlorine (oxidation) ammonia to nitrogen gas which will result in the reduction of the amount of chlorine rest. At the point where the least amount of residual chlorine concentration is what called "optimum point". If after going through optimum point and additional chlorine is continued, free chlorine will work as a disinfectant [15].

Based on the above, it can be known that the addition of chlorine in the phase before the optimum point is chlorine consumed needed (chlorine demand) that is the amount of chlorine needed to oxidize all organic material one of which is ammonia. When the optimum point that has been reached, then the amount of remaining chlorine that exists will decrease because, it was used to react with chlorine and N_2 gas is formed, it can be said that the chlorine dose at that point was the right dosage for removing ammonia. Whereas, after through the optimum point, the addition of chlorine will produce free chlorine which free chlorine will no longer oxidize ammonia but rather will function as a disinfectant. The application of sodium hypochlorite can be draw as like flow diagram in the Fig 8 below:

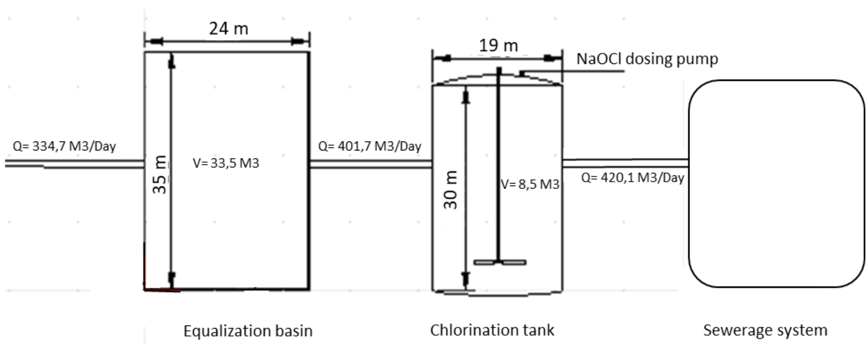

Fig 8. Flow process for chlorination treatment using NaOCl 9% *(source: Design drawing)*.

4 Conclusions

In this study, the effectiveness of a sodium hypochlorite in wastewater for chlorination process and the residual chlorine after treatment were investigated. The results proved that the sodium hyphochlorite exposure reduces ammonia concentration in water samples. The results also suggested that the dose variations of sodium hypochlorite influence ammonia removal efficiencies. Also, mostly the total residual chlorine increases with the increasing sodium chlorine dose. Then, for the effective sodium hypochlorite 9% solution dose was (110 mg/L) applied in the experiments resulted can remove 82,2% the ammonia concentration from 50 mg/L to 8,9 mg/L and produce residual chlorine which the amount was 0,72 mg/L residual chlorine. Recommendation for future research, experiments should be carried out with less doses and smoothly range.

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