

COMPARISON OF ANALYSIS RESULTS OF pH, TSS, COD AND AMMONIA IN INDUSTRY WASTEWATER WITH SPARING AND SNI METHODS

Dessy Nur Indryastuti^{a*)}, Ani Iryani^{a)}, Muhammad Fathurrahman^{a)}

^{a)}Chemistry Study Program, Faculty of Mathematics and Natural Sciences, Pakuan University, Bogor, 16129, Indonesia

^{*)}Corresponding Author : dessy.nindryastuti@gmail.com

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ABSTRACT

Sparing is a development of sensor technology to monitoring wastewater quality continuously and online, so it can be done in real time. Wastewater quality monitoring carried out in the laboratory using the SNI method still has several drawbacks, including large analysis costs, long analysis time and the use of chemicals that are not environmentally friendly. This study aims to determine the differences in the results of the analysis of the Sparing method with SNI on the parameters of pH, TSS, COD, and ammonia in the EWTP wastewater of PT "X" using statistical processing through the F-test and T-test. The research stages include sampling, sample storage and analysis in the laboratory. Based on the results of the study, it can be concluded that the differences in the method of Sparing analysis and SNI are not significantly different to the pH parameters in the measurement range 6.77 - 6.88; TSS in the measurement range 9.486 - 12.343 mg/L; COD in the measurement range of 55.402 - 59.274 mg/L and ammonia in the measurement range of 0.368 - 0.405 mg/L. This proves that the Sparing method can replace the SNI method for routinely monitoring the quality of EWTP wastewater of PT "X".

Keywords: Online Monitoring, Sparing, Wastewater Analysis Method, Wastewater Sensor

1. INTRODUCTION

Industrial waste is one of the main pollutants in the water. These pollutants can pollute the environment in the form of solutions, colloids, or other particle forms. Therefore, given the importance and magnitude of the impact on the environment, an appropriate method is needed to treat water [1]. Every activity that generates wastewater is required to dispose of its wastewater with quality in accordance with the established quality standards and also must carry out environmental monitoring at least once a month by an accredited laboratory [2]. One of the consequences from the Covid-19 Pandemic is the restriction of human mobility to minimize the spread of the virus. Of course this has an impact on laboratory performance. In addition, monitoring the quality of wastewater in the laboratory using the SNI method has many shortcomings, i.e. including large analysis costs, long analysis time, and the use of chemicals that are not environmentally friendly.

Sparing is one of the applications of technology 4.0 in the wastewater treatment installation unit. The

monitoring system for the quality of wastewater discharged into the environment based on the same technology is expected to be an important step of strategic value to be implemented in order to maintain environmental stability and a sustainable industry. A more serious and intensive monitoring approach has been carried out with the issuance of the Minister of Environment and Forestry Regulation Number 93 of 2018 concerning Continuous and Online Monitoring of Wastewater Quality (called Sparing).

Monitoring the quality of wastewater with Sparing in real time and online is a solution to minimize the risk of sample takers and laboratory analysts being exposed to viruses and reduce the risk of human error during the sampling process, sample storage and preservation, as well as during analysis in the laboratory. In addition, with the support of accurate digital sensors and qualified information technology, it will provide information directly to supervisory agencies or supervisors as well as internal industry so that they can quickly find out the quality of the wastewater produced. Monitoring results can

provide an early warning for internal industry to quickly make corrective steps in the production process and pollution control unit if the indicator parameters have exceeded the quality standard. Meanwhile, in the terms of institutions or related agencies, they can immediately provide guidance and warnings to industries that violate the provisions, as well as obtain a more comprehensive and more comprehensive collection of monitoring data that can be used as the basis for making environmental policies [3].

With the differences in the working principles of the two wastewater quality monitoring methods, the researcher aims to determine the difference in the values produced by the Sparing analysis method with SNI on the parameters of pH, Total Suspended Solid (TSS), Chemical Oxygen Demand (COD), and also ammonia ($\text{NH}_3\text{-N}$) in the Effluent Water Treatment Plant (EWTP) wastewater sample of PT "X" by using statistical processing through the F-test and T-test.

2. METHODS

The sample used is wastewater taken from EWTP of PT "X" once for 30 consecutive days at the same time. The sampling time chosen was 11.00 AM which is a labor-intensive activity. Sampling was carried out using a sampling bottle and a 10 liter jerry can holder. After that the samples were tested for homogeneity before being distributed for analysis using the Sparing and SNI methods. If the sample is declared homogeneous, then the sample is analyzed based on the parameters of pH, TSS, COD, and ammonia using SNI, as well as direct reading of the four parameters above using the Sparing tool for seven repetitions.

The data obtained from the research results were statistically analyzed using Microsoft Excel with the F-test (Fisher's test). If the results showed no significant difference, then continued with the T-test (Student's t-test). Comparison of the results of the two analytical methods in this study used the following hypothesis :

H_0 = Sparing analysis method with SNI does not have a significant difference on parameters of pH, TSS, COD, and ammonia in the EWTP wastewater sample of PT "X".

H_1 = Sparing analysis method with SNI has a significant difference on the parameters of pH, TSS, COD, and ammonia in the EWTP wastewater sample of PT "X".

2.1. Tools

Tools used in study i.e. pH meter, beaker, flask, spray flask, analytical balance, magnetic stirrer, desiccator, volumetric pipette, oven, dropper pipette, watch glass, tempered glass cup, tweezers, vacuum, erlenmeyer, UV-VIS spectrophotometer, hot plate, cuvette, digestion vessel (16 mm x 100 mm culture tube), heating block, micro burette, COD reactor and Sparing.

2.2. Ingredients

Ingredients used in study i.e. buffer pH 4, pH 7 and pH 10, distilled water, whatman filter paper number 41, potassium hydrogen phthalate standard solution ($\text{HOOC}_6\text{H}_4\text{COOK.KHP}$), phenol solution ($\text{C}_6\text{H}_5\text{OH}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sulfuric acid (H_2SO_4), sodium nitroprusside ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$), ammonia standard ocean and oxidizing solution.

2.3. Procedure Analysis

2.3.1. pH

pH test is done by the method of SNI 6989.11:2019. Before use, the pH meter is calibrated using a buffer solution of pH 7, pH 4 and pH 10. When the calibration has shown the appropriate results, the pH meter is ready for use. Next, the pH meter electrode was rinsed with distilled water three times and wiped using a tissue, then the electrode was immersed in the test sample until it showed a stable result [4].

2.3.2. Total Suspended Solid (TSS)

TSS test is done by the method of SNI 6989.3:2019, i.e. the suspension contained in 100 mL of the sample was filtered using filter paper with the help of a vacuum. The residue retained on the filter paper was dried in an oven at a temperature of 103 - 105 °C until it reached a constant weight. The increase in residual weight represents Total Suspended Solids (TSS) [5].

2.3.3. Chemical Oxygen Demand (COD)

COD test is done by the method of SNI 06-6989.2:2009, i.e. a total of 2.5 mL of sample was added with 1.5 mL of potassium dichromate and 3.5 mL of concentrated sulfuric acid then refluxed closed for 2 hours at a temperature of 150 °C and then measured by a spectrophotometer at a wavelength of 420 nm, with a range of COD values less than or equal to 90 mg/L [6].

2.3.4. Ammonia (NH₃-N)

Ammonia test is done by the method of SNI 06-6989.30-2005, i.e. a total of 25 mL of the sample was pipetted, then put into an erlenmeyer. Added 1 mL of phenol solution, 1 mL of sodium nitroprusside and 2.5 mL of oxidizing solution, then homogenized. Waited for 1 hour for the formation of color and then measured by a spectrophotometer at a wavelength of 640 nm [7].

2.3.5. Sparing

Sparing tools that have been calibrated can be used directly by immersing the multiprobe sensor from the Sparing tool into the sample until the entire sensor is submerged. The tool will read the levels of pH, TSS, COD, and ammonia automatically. Wait a few seconds for the reading to stabilize and the measured value will automatically appear on the monitor screen, then record the measured value obtained [8].

3. RESULTS AND DISCUSSION

3.1. Homogeneity Test Results

Based on the results of the homogeneity test of wastewater on the parameters of pH, TSS, COD, and ammonia for 30 days of observation, the value of S_s 0.3 δ can be concluded so that the samples of EWTP PT "X" wastewater are declared homogeneous and can be compared with each other. The homogeneous samples were then stored at room temperature for further analysis of the parameters pH, TSS, COD, and ammonia using the Sparing and SNI methods.

3.2. Low Level COD Linearity Test Results

Based on the results of the homogeneity test, the COD value is known to be in the range of ± 60 mg/L, so that the linearity test is carried out with low levels of COD less than 90 mg/L and standard solution concentration 0; 10; 20; 40; 60; 80; and 90 mg/L of potassium hydrogen phthalate mother liquor (KHP) 500 mg O₂/L. Then the absorbance of each standard solution was measured with a spectrophotometer UV VIS at a wavelength of 420 nm. Then the absorbance and concentration data obtained are plotted into a calibration curve to obtain the equation as shown in Figure 1.

Based on the results of the linearity test that has been carried out, the correlation coefficient (r) is 0.9994 and the determination coefficient (R^2) is 0.9988 with the linear regression equation $y = -0.0009x + 0.1287$, so it can be concluded that the

curve value calibration for testing low COD values meets the acceptance requirements in accordance with the provisions stipulated by SNI 6989.2-2019, i.e. $r \geq 0.995$. This means that the spectrophotometric COD method with a low COD value of less than 90 mg/L has good linearity.

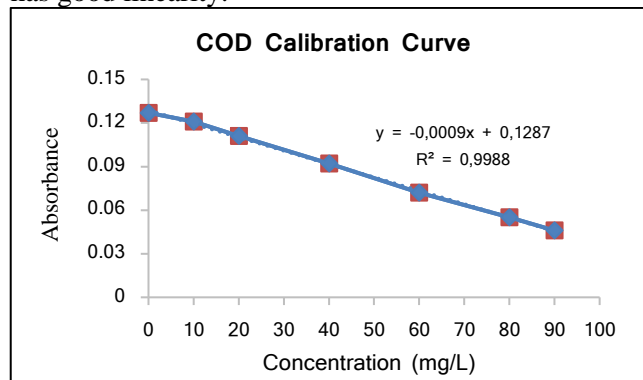


Figure 1. Low COD Calibration Curve

3.3. Ammonia Linearity Test Results

Standard solution with a concentration of 0.00; 0.10; 0.20; 0.30; 0.50; and 0.60 mg/L of standard 10 mg/L ammonia solution was measured using a UV VIS spectrophotometer at a wavelength of 640 nm. Then the absorbance and concentration data obtained are plotted into a calibration curve to obtain the equation as shown in Figure 2.

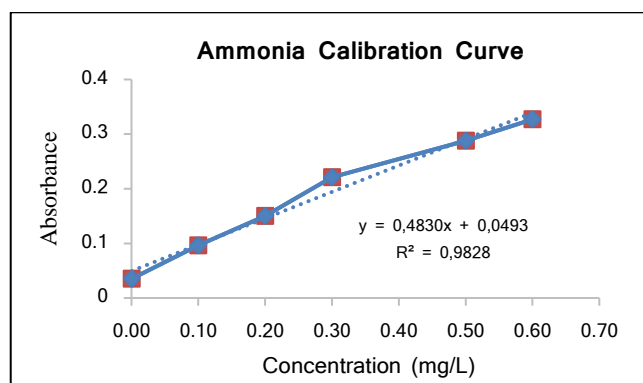


Figure 2. Ammonia Calibration Curve

Based on the results of the linearity test that has been carried out, the correlation coefficient (r) is 0.9914 and the coefficient of determination (R^2) is 0.9828 with the linear regression equation $y = 0.4830x + 0.0493$, so it can be concluded that the calibration curve value for the ammonia test, it meets the acceptability requirements in accordance with the provisions stipulated by SNI 06.6989.30-2005, i.e. $r \geq 0.97$. This means that the spectrophotometric ammonia method has good linearity.

3.4. Wastewater Analysis Results

The results of the research that has been carried out for 30 days of observation by measuring the parameters pH, TSS, COD, and ammonia using the Sparing and SNI methods can be seen in Table 1.

Table 1. PT "X" EWTP Wastewater Analysis Results

Parameters	Sparing Method	SNI Method
pH	6,83	6,82
TSS	10,383	10,215
COD	57,460	57,633
Ammonia	0,387	0,389

Precision is degree to which the repetition of the analysis gives the same data. Precision was measured using the standard deviation (SD) of the repeated analysis results to produce the relative standard deviation (%RSD) [9]. Based on the results of precision tests on the parameters of pH, TSS, COD and ammonia which were carried out for 30 days of observation, both analytical methods, namely Sparing and SNI, showed the value of %RSD < 2/3 CV Horwitz. So it can be concluded that the analysis of parameters pH, TSS, COD, and ammonia has a good precision value.

Accuracy is a measure of how close the value of the average measurement results obtained from a number of repeated measurements is to the true value. The accuracy test method in this study is done indirectly by comparing two methods that have different principles on testing the same sample [10]. In this case, the results of the analysis using the Sparing method are the measured values, while the results of the analysis using the SNI method are the correct values. The difference between the measurement results and the correct value of the reference method is an indicator of inspection inaccuracy (bias). The results of the accuracy test can be seen in Table 2.

Table 2. Accuracy Test Results

Parameters	% Bias	% Accuracy
pH	-0,12	100,12
TSS	-1,64	101,64
COD	0,30	99,70
Ammonia	0,60	99,35

If we viewed from the Table 2, the smaller the bias, the higher the resulting accuracy. Based on the results of research for 30 days of observation, it can be

concluded that the % accuracy of the parameters pH, TSS, COD and ammonia shows good results and is included in the terms of acceptance, % accuracy is 90 - 110% and bias < 10% [11]. This means that the Sparing method can produce accurate values.

3.5. Comparison Results of Wastewater Analysis of Sparing Method and SNI

The analysis data obtained from the Sparing and SNI methods were further analyzed by processing statistical data using the F-test and T-test, the aim was to see a comparison of the resulting values between the two methods. The conclusion of the F-test in this study is to compare the values of F_{count} and F_{table} obtained with a 95% confidence level. If $F_{count} \leq F_{table}$ then H_0 is accepted and H_1 is rejected, otherwise if $F_{count} \geq F_{table}$ then H_0 is rejected and H_1 is accepted. While the conclusion on the T-test is to compare the values of t_{count} and t_{table} obtained with a 95% confidence level. If $t_{count} \leq t_{table}$ then H_0 is accepted and H_1 is rejected, otherwise if $t_{count} \geq t_{table}$ then H_0 is rejected and H_1 is accepted. The results of the F-test and T-test for 30 days of observation can be seen in Tables 3 and 4.

Table 3. F-Test Results

Parameters	F-Test		
	F_{count}	F_{table}	Conclusion
pH	0,8791	3,3541	not significantly different
TSS	0,7800	3,3541	not significantly different
COD	0,2932	3,3541	not significantly different
Ammonia	0,6550	3,3541	not significantly different

Table 4. T-Test Results

Parameters	T-Test		
	T_{count}	T_{table}	Conclusion
pH	1,2268	$\pm 2,0017$	not significantly different
TSS	0,9847	$\pm 2,0017$	not significantly different
COD	- 0,7540	$\pm 2,0017$	not significantly different
Ammonia	- 1,1622	$\pm 2,0017$	not significantly different

Based on Tables 3 and 4 above, the results of the calculation of the F test and T test of the parameters pH, TSS, COD and ammonia show the values of $F_{count} \leq F_{table}$ and $T_{count} \leq T_{table}$ so that it can be concluded that H_0 is accepted and H_1 is rejected. This means that the difference between the Sparing analysis method and SNI is not significantly different for the parameters of pH, TSS, COD and ammonia in the PT "X" EWTP wastewater sample.

4. CONCLUSION

Based on the results of the study, it can be concluded that the Sparing analysis method with SNI is not significantly different from the pH parameter in the measurement range of 6.77 - 6.88; TSS 9,486 - 12,343 mg/L; COD 55,402 - 59,274 mg/L; and ammonia 0.368 - 0.405 mg/L. This proves that the Sparing method can replace the SNI method for routinely monitoring the quality of PT "X" EWTP wastewater.

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