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Research paper

Determination of Chemical Oxygen Demand (COD) Concentration in Domestic Wastewater Using UV-Vis Spectrophotometry Method Based On The Effect Of Reflux Time And Preservation Time

Penentuan Konsentrasi *Chemical Oxygen Demand* (COD) Dalam Air Limbah Domestik Menggunakan Metode Spektrofotometri UV-Vis Berdasarkan Pada Pengaruh Waktu Refluks Dan Waktu Pengawetan

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ABSTRACT

The purpose of determining Chemical Oxygen Demand (COD) in samples of domestic wastewater is to determine the effect of variations in the reflux process time which is set to 0, 30, 60, 90, and 120 minutes as well as with variations in the testing time which are set to 0, 3, and 7 days. Determination of LOD and LOQ using a UV-Vis Spectrophotometer was also carried out and the regression equation y = 0.0003x + 0.0066 with a coefficient of determination (R^2) was 0.998 with LOD and LOQ values respectively 40.0416 mg O_2/L and 133.4721 mg O_2/L. Determination of the effect of reflux time and preservation time on COD levels was carried out statistically, namely the normality test (Kolmogorov-Smirnov Test) and homogeneity test (Levene Test) ending with a two-way ANOVA test with a probability or significance value of the inlet and outlet samples of 0.000 < 0.05. Reflux time affects COD levels, the longer the reflux time, the higher and more stable COD levels. Preservation time affects the decrease in COD levels, which is the longer the preservation time, the greater the decrease in COD levels.
Keywords: *Wastewater, Spectrophotometer, Chemical Oxygen Demand, Time variation*

PENDAHULUAN

Life is composed of various important elements, one of which is water. Without water, at this time there would most likely be no such thing as life. Water is also the largest unit that composes the body of living things as well as the human body which contains water for approximately 70% of the total body, therefore if the need for water is not fulfilled it will have a major impact on health and social vulnerability. Water is a universal solvent that can dissolve many substances or compounds compared to other liquids, causing water to be very susceptible to pollution. Therefore, changes in the physical, chemical, and biological properties of water will have very

detrimental consequences for the environment and living things.

Hazards or health risks associated with water pollution can be divided into two categories, namely direct hazards and indirect hazards. Direct hazards to human/community health can occur due to consumption of polluted water (poor quality), either directly or through food, and due to the use of polluted water for use in various other daily activities. Various effects of industrial and agricultural activities can also cause public health hazards. Indirect hazards can occur, one of which is the result of consuming fishery products where these products accumulate harmful substances or pollutants (Said, 2008).

Quoted from National Geographic Indonesia, one of the main causes or sources of water pollution in Indonesia mostly comes from domestic or household waste. Domestic waste is very influential in the decline in water quality. According to a 2016 survey by the Directorate General of Human Settlements, the average water consumption of urban households in Indonesia is 144 liters/person per day, while Indonesia's minimum basic needs are 70 liters/person per day (BPS, 2020).

The availability of clean water management is needed to overcome the problem of water pollution, following what has been stipulated in the Environmental Pillar's Sustainable Development Goals (TPB) in the sixth goal point, namely "ensuring the availability and management of clean water and proper sanitation". The water right has also been regulated in the 1945 Constitution in Article 33 paragraph 3. The international declaration in the UN Declaration of Human Rights of Water, in general, has also explained that human rights regarding water are needed to ensure human life with dignity (UN, 2010).

Among the many water quality parameters, COD is one of the most decisive parameters. The higher levels of COD in water can cause various kinds of diseases for humans due to the presence of organic pollutants in high amounts, and the number of microorganisms both pathogenic and non-pathogenic. Chemical Oxygen Demand (COD) can cause the dissolved oxygen content in water bodies to be low or even depleted. This study focuses on determining COD parameters with variations in the reflux/digestion process (0, 30, 60, 90, and 120 minutes) and preservation time (0, 3, and 7 days) to determine whether or not there is an effect on the concentration value. COD is obtained as well as knowing the levels of COD inlet and outlet in the wastewater treatment process. Chemical Oxygen Demand (COD) is defined as the amount of certain oxidant (mg O_2) that reacts with the sample under controlled conditions or the amount of oxygen required in the process of chemically oxidizing organic substances in one liter of the water sample. COD levels in domestic wastewater can be determined using the closed reflux method by SNI 6989.2:2009. (BSN, 2019) in addition, the 2017 APHA method section 5220-D can also be used for COD testing utilizing closed reflux testing using the columnometric method, namely by reducing dichromate ions Cr2O72- to chromic ions (Cr^{3+}) (Baird, et.al, 2017).

METHODOLOGY

Materials and tools

The tool used in this method is a set of UV-Vis Spectrophotometer instruments (Thermo Scientific), COD Reactor (HACH), oven (Biden), and water sampler horizontal. While the materials used include samples of domestic wastewater, chemicals include potassium hydrogen phthalate ($C_8H_5KO_4$) (Merck), sulfuric acid pro analysis (H_2SO_4 p.a) (Merck), silver sulfate (Ag_2SO_4) (Merck), potassium dichromate ($K_2Cr_2O_7$) (Merck), mercury sulfate ($HgSO_4$) (Merck) and aquadest.

Research procedure

Preparation

Domestic wastewater samples that have been taken are added with a solution of H_2SO_4 p.a. until pH <2. The sample was transferred into a glass bottle and stored at 4 ^oC. with maximum storage time 7 days.

Calibration curve

The standard solution of COD 1000 mg O_2/L was pipetted as much as 0 each; 2.5; 5.0; 10.0; 15.0; 20.0; 25.0; 30.0; 35.0 and 40 mL into a 50 mL volumetric flask. The distilled water was added until the calibration mark was then homogenized after wiping. The blank solution and each standard series solution were pipetted as much as 2.5 mL into the test tube/vial. A total of 1.5 mL of digestion solution and 3.5 mL of H_2SO_4 reagent solution were added to the test tube. Cover and shake gently until homogeneous. The solutions were placed on a heater that has been heated at a temperature of 150 °C and refluxed for 2 hours. The standard solution which has been refluxed

is then cooled to room temperature and the absorbance value is measured 3 times at a wavelength of 600 nm. The calibration curve is drawn and the equation of a straight line is determined. The test of standart is repeated if the correlation coefficient (r) < 0.995 and tested until the value of r is obtained to > 0.995.

Determination of COD levels in domestic wastewater samples

A total of 2.5 mL of the test sample was put into the test tube/vial. A total of 1.5 mL of digestion solution and 3.5 mL of H_2SO_4 reagent solution were added to the test tube. Cover and shake gently until homogeneous. Place the prepared sample in a heater (COD reactor) which has been heated at a temperature of 150 °C and refluxed with time variations of 0, 30, 60, 90, 120 minutes. The test sample which has been refluxed is then cooled to room temperature. The test sample which has been refluxed is cooled to room temperature to prevent the formation of a precipitate. Occasionally the sample cap is opened to prevent gas pressure if necessary. The suspension is allowed to settle and it is ensured that the part to be measured is completely clear. The sample was measured for absorption at a predetermined wavelength of 600 nm with 3 readings. COD levels were calculated based on the linear equation of the calibration curve. The determination of COD in the sample was carried out again with variations in the preservation time of samples 3 and 7 days.

Statistic test

Variations of reflux samples 0, 30, 60, 90, and 120 minutes which have been examined in the same laboratory, by the same technician, using the same equipment, but at different times (days) are 0, 3, and 7 days. Formulated a hypothesis and then calculated the results of statistical analysis to determine the hypothesis. Statistical tests were carried out by looking for normality and homogeneity values before the two-way ANOVA test was performed.

RESULTS AND DISCUSSION

Determination of COD Concentration

In general, the level of wastewater pollution can be seen from the concentration of COD. The level of wastewater pollution usually depends on the number of components in the wastewater such as the amount of ammonia, suspended solids, heavy metals or COD. In general, the level of COD concentration in municipal wastewater is usually less than 1000 mg/L (Tran, 2015). The COD parameter is one of the most important parameters that can indicate the level of contamination of organic compounds in the water system (Zhang, 2018).

The principle of determining Chemical Oxygen Demand (COD) using a closed reflux method by photometry or spectrophotometry is by oxidizing organic compounds in domestic wastewater using a strong oxidizing agent in the form of potassium dichromate ($K_2Cr_2O_7$) in combination with sulfuric acid (H_2SO_4) and the addition of silver sulfate ($AgSO_4$). and mercury sulfate ($HgSO_4$). Oxidation takes place during the closed heating (reflux) process for a certain time at a temperature of 150°C. Reflux equipment is used to avoid any reduction in sample size caused by heating (Mulyati, 2020). Oxidation of organic substances will follow the following reaction (Wayne, 1997).

$$2C_8H_5KO_4 + 10K_2Cr_2O_7 + 41H_2SO_4 \rightarrow 16CO_2 + 46H_2O + 10Cr_2(SO_4)_3 + 11K_2SO_4$$

$$16\ C^{1/4} - 60e^- \rightarrow 16\ C^{IV} \text{ (Oxidation)}$$

$$20\ Cr^{VI} + 60e^- \rightarrow 20\ Cr^{III} \text{ (Reduction)}$$

$C_8H_5KO_4$ (Agent pereduksi), $K_2Cr_2O_7$ (Agent pengoksidasi)

A strong oxidizing agent ($Cr_2O_7^{2-}$) serves to oxidize organic compounds to carbon dioxide and water under acidic conditions. Silver sulfate ($AgSO_4$) functions as a catalyst to promote the oxidation of certain organic compounds and mercury sulfate ($HgSO_4$) to reduce interference from the oxidation of chloride ions (Cl^-) or prevent the precipitation of Ag^+ catalyst as AgCl. The amount of oxidant required (COD) expressed in oxygen equivalents (mg O_2/L) was measured using a UV-Vis spectrophotometer. If the value or levels of COD are in the range of values of 100 to 900 mg/L, measurements are made using a wavelength of 600 nm. If the COD value is in the range of values of 90 mg/L, the determination is carried out using a wavelength of 420 nm (BSN, 2019. The use of the UV-Vis Spectrophotometry method for measuring the COD concentration is an indirect method. The selectivity and accuracy of this method are limited by the presence of physical

disturbances such as turbidity (Ma, 2017). Thus, the condition of the sample before measurement must be in a condition that is free from interfering particles or the solution is in a clear condition

Determination of COD in domestic wastewater in this study added a variation in the form of differences in reflux time and preservation time to determine the effect. Reflux time variations used were 0, 30, 60, 90, and 120 minutes with identical reflux temperatures at 150°C, while variations in preservation time used were 0, 3, and 7 days. The results of determining COD in the presence of these two variations can be seen in Figure 1 for the inlet sample and Figure 2 for the outlet sample.

Meanwhile, the results of testing on waste samples with variations in preservation time and reflux time are presented in Tables 1 and 2.

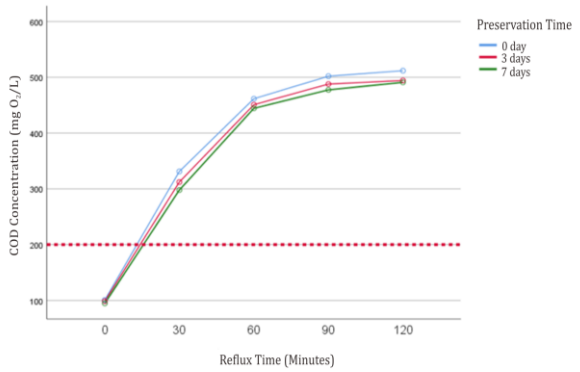

Figure 1. The relationship between test variation and COD concentration in the sample inlet

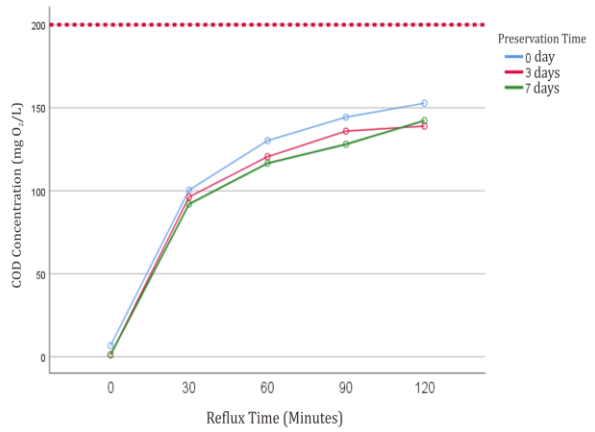

Figure 2. The relationship between test variation and COD concentration in the sample outlet

Table 1. The results of determining the COD of the inlet sample

Preservation Time (day)	Reflux Time (minutes)					Quality standards
	0 (mg O_2/L)	30 (mg O_2/L)	60 (mg O_2/L)	90 (mg O_2/L)	120 (mg O_2/L)	(mg O_2/L)
0	100.6984	331.1746	461.5556	501.9683	511.8095	
3	98.6349	312.1270	450.8571	487.8413	494.3492	200.00
7	94.6667	297.8413	444.3492	477.3651	491.0159	

Tabel 2. The results of determining the COD of the outlet sample

Preservation Time (day)	Reflux Time (minutes)					Quality standards
	0 (mg O_2/L)	30 (mg O_2/L)	60 (mg O_2/L)	90 (mg O_2/L)	120 (mg O_2/L)	(mg O_2/L)
0	6.7302	100.3810	130.2222	144.3492	152.7619	
3	1.1746	96.2540	120.5397	135.9365	138.9524	200.00
7	1.0159	91.9683	116.5714	128.0000	142.2857	

The existence of variations in reflux time is assumed to affect the efficiency level of oxidation by potassium dichromate, which according to Wayne (1997) the level of oxidation efficiency of most organic compounds occurs according to the procedure specified in the APHA 5220-D method, namely with closed reflux treatment for 120 minutes whose efficiency is ranged from 90-100%. Therefore, the increase in COD levels that occurs at each time variation can be said to be an increase in the oxidation efficiency of organic compounds.

Preservation affects COD levels which are assumed to be due to the metabolic activity of microorganisms that can change the levels of nitrate (NO_3), nitrite (NO_2), ammonia (NH_3), organic N, organic phosphate, sulfate, and reduce phenol levels as well as indicators of organic substances such as BOD. , COD, DO, and permanganate values. In addition, pickling can cause the absorption of colloids, solutes, and/or suspended by the surface on which the sample container is placed (Inge, 2018). To further strengthen the statement of the effect of variations in reflux time and curing time, it can be seen in the results of statistical tests.

Statistical test on the effect of reflux time variation and curing time on the concentration of COD in the sample

The research data must be validated first before making a decision/conclusion about the results. One form of the validity of the research data is by conducting a normality test in the form of a statistical test. Based on the results of the calculation of the normality test using the Kolmogorov-Smirnov method for each sample (inlet and outlet) it is presented in Table 3 while the standard distribution of residuals in

the inlet and outlet samples is presented in Figures 3 and 4.

Table 3. Kolmogorov-Smirnov Normality Test on samples

Parameter	Standardized Residual for COD	
	Inlet	Outlet
Statistic	0.068	0.069
df	105	105
Sig.	0.200*	0.200*

The statistical values given in Table 3 for both the inlet and outlet samples have a significance value of 0.200> 0.05(α) with Liliefors adjustment, so the sample data is normally distributed. Meanwhile, for the standard distribution of residuals in the sample data of inlet and outlet which shows distributed data, it can be seen in Figures 3 and 4.

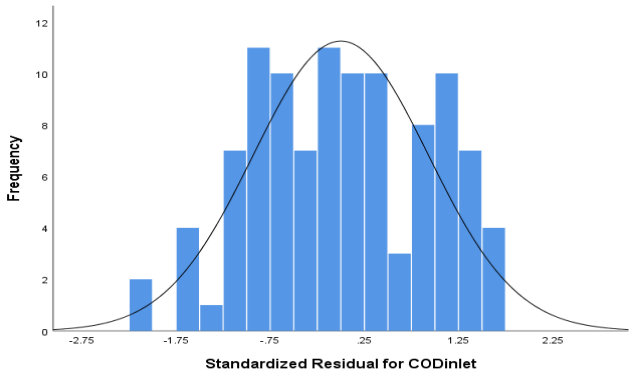

Figure 3. Standard residual inlet sample

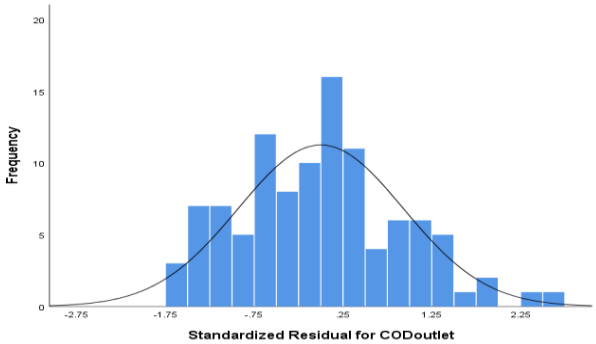

Figure 4. Standard residual outlet sample

Based on Table 4 shows that the data from the test results of the domestic wastewater inlet sample is assumed to be homogeneous based on the mean levene statistic of 1.197 and the probability or significance value (Sig.) is 0.292. Meanwhile, the data from the test results for samples of domestic wastewater outlets is assumed to be homogeneous based on the mean levene statistic of 0.710 with a probability or significance value (Sig.) of 0.759. Because the test data have been declared normal and homogeneous, it can be continued with a two-way ANOVA statistical analysis to determine whether or not there is an effect of reflux time variation and preservation time on the determination of Chemical Oxygen Demand (COD) levels.

Table 4. Homogeneity test

		Sampel Inlet				Sampel Outlet			
		Levene Statistic	*df1*	*df2*	*Sig.*	*Levene Statistic*	*df1*	*df2*	*Sig.*
Kadar COD Inlet (Y)	*Based on Mean*	1,197	14	90	0,292	0,710	14	90	0,759
	Based on Median	0,915	14	90	0,546	0,488	14	90	0,934
	Based on Median and with adjusted df	0,915	14	79.150	0,547	0,488	14	68.951	0,932
	Based on trimmed mean	1,196	14	90	0,293	0,667	14	90	0,800

Following the results of the two-way ANOVA test, the probability or significance (Sig.) results for each variation are the reflux time variation and the curing time of 0.000 < 0.05 (α) with R-Squared values of 1.0 and 0.997 which state a strong correlation. This value indicates that the variation of reflux time and curing time affects the concentration of COD obtained simultaneously.

CONCLUSION

Based on the results of the study showed that the longer the reflux time, the higher and more stable COD levels. Preservation time affects the decrease in COD levels, where the longer the preservation time the greater the decrease in COD levels.

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