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DEVELOPMENT OF COD (CHEMICAL OXYGEN DEMAND) ANALYSIS METHOD IN WASTE WATER USING UV-VIS SPECTROPHOTOMETER

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Abstract. The COD (Chemical Oxygen Demand) analysis method based on the Indonesian National Standard (SNI) is a revision of SNI 06-6989.2-2004, Water and wastewater - Part 2: Method of testing for chemical oxygen demand (COD) with closed reflux spectrophotometrically. This SNI uses references from international standard methods, namely Standard Methods for the Examination of Water and Wastewater, 21st Edition, editor of LS Clesceri, AE Greenberg, AD Eaton, APHA, AWWA and WEF, Washington DC, 2005, Methods 5220 D (Closed Reflux, Colorimetric Methods). The purpose of this study was to validate the total method for testing chemical oxygen demand (COD) in water and wastewater with the reduction of Cr_2O_7 2- spectrophotometrically in the range of COD values of 100 mg / L to 900 mg / L measurements were made at a wavelength of 600 nm. and COD values less than or equal to 90 mg / L measurements were made at a wavelength of 420 nm. The results showed that the method SNI 06-6898.2- 2009 has good validation results including the r results obtained from the calibration curve equation of 0.998, a precision of 1.82%, an accuracy of 98.25% and LOD and LOQ of 12.27 mg / L and 25, 61 mg / L.

Keywords: wastewater; COD analysis; UV-VIS spectometry; validation, LOD

I. INTRODUCTION

Water is one of the natural resources which has a very important function for human life, as well as for advancing the general welfare so that it is the basic capital and the main factor of development. The main need for the implementation of good health is the availability of adequate water in terms of quantity and quality, namely meeting the requirements for cleanliness and safety. This water must also be available continuously, attractive and acceptable to the community in order to encourage people to use it **[1]**. Increased human activities will cause various problems, one of which is water pollution in water sources because it receives a pollution load that exceeds its carrying capacity. Pollution that causes a decrease in water quality can come from point sources and non-point sources. Centralized waste such as industrial waste, livestock business waste, hotel waste, and hospital waste. Meanwhile, the waste is scattered, such as agricultural waste, plantation waste and domestic waste **[2]**.

Domestic waste is waste originating from bathrooms, latrines, kitchens, washing clothes, washing household appliances, pharmacies, restaurants and so on quantitatively. This waste consists of organic substances in the form of solid or liquid, hazardous and toxic materials (B3), dissolved salts, and bacteria, especially the fecal coli, pathogenic bodies, and parasites **[3]**.

The COD analysis method based on the Indonesian National Standard (SNI) is a revision of SNI 06-6989.2-2004, Water and wastewater - Part 2: Method of testing for chemical oxygen demand (COD) with closed reflux spectrophotometrically. This SNI uses references from international standard methods, namely Standard Methods for the Examination of Water and Wastewater, 21st Edition, editor of LS Clesceri, AE Greenberg, AD Eaton, APHA, AWWA and WEF, Washington DC, 2005, Methods 5220 D (Closed Reflux, Colorimetric Methods) **[4]**.

This SNI has been tested in testing laboratories in the framework of validating and verifying the method and consensed by the 13-03-S1 Technical Sub-Committee, Water Quality from the 13-03 Technical Committee, Environmental Quality and Environmental Management with related parties. This SNI has been agreed and approved in a consensus meeting with meeting participants representing producers, consumers, scientists, technical agencies and related governments on 29 October 2008 in Serpong, Tangerang - Banten and has been through a poll on 18 March 2009 to 18 June 2009, with the final RASNI result. With the stipulation of SNI 06-6898.2-2019, the application of SNI 06-6989.2-2004 is declared invalid. SNI users should be able to research SNI validation related to this method, so they can always use the latest edition of SNI **[5]**.

The purpose of this research is to validate the total method that must be done for each method of analysis, either

Volume 03, Number 02, September 2020, Page 35-38
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for new methods or just repetition based on literature. Method validation has the main objective of demonstrating the reliability of a particular method (European Medicines Agency, 2011). This COD validation method is used for testing chemical oxygen demand (COD) in water and wastewater with spectrophotometric reduction of Cr_2O_7 2- in the COD value range of 100. mg / L up to 900 mg / L measurements were made at a wavelength of 600 nm and COD values less than or equal to 90 mg / L measurements were made at a wavelength of 420 nm **[6]**.

II. RESEARCH METHODS

Tools and Materials

The tools used in this study were DO bottles, incubation cabinets or water coolers, temperature 20 ° C ± 1 ° C, dark; bottles from glass 5 L - 10 L; volumetric pipettes 1.0 mL and 10.0 mL; 100.0 mL volumetric flask; 200.0 mL and 1000.0 mL; PH meter; DO meter is calibrated; shaker; blender; oven; and analytical scales. For COD, visible spectrophotometer (400 nm to 700 nm), cuvette; digestion vessel, burette; volumetric flask 50.0 mL; 100.0 mL; 250.0 mL; 500.0 mL and 1000.0 mL; 5.0 mL volumetric pipette; 10.0 mL; 15.0 mL; 20.0 mL and 25.0 mL; beaker glass; magnetic stirrer. The materials used in this study were $K_2Cr_2O_7$, H_2SO_4, $HgSO_4$, Ag_2SO_4 powder, NH_2SO_3H (Sulfamic Acid), demineralized water.

Analysis of Cod in Wastewater Using a Uv-Vis Spectrophotometer

The research method includes the preparation of reagents, stock standard solutions and working standard solutions, optimization of detection parameters on the UV-vis spectrometer and validation of the analysis method. Validation of the analysis method includes parameters of the calibration curve, precision, accuracy, and recovery test.The validation of the COD analysis method carried out is the total validation which refers to SNI 6989.2: 2009. Validation parameters include linearity, accuracy, precision, LOD and LOQ.

1) Taking COD test samples

Preparation of test samples

Who is the test sample, namely by a) homogeneous the test sample; b) wash digestion vessel and cover with 20% H_2SO_4 before use; Preservation of test samples If the test sample cannot be tested immediately, then the test sample is preserved by adding concentrated H2SO4 until the pH is less than 2 and stored in a cooler at a temperature of 4 ° C ± 2 ° C with a maximum recommended shelf life of 7 days. 3.5 Preparation of working solutions Create a work solution series from the KHP main solution with 1 (one) blank and at least 3 proportionally different levels that are in the measurement range.

Digestion procedure

pipette the volume of the test sample or working solution, add the digestion solution and add a sufficient sulfuric acid reagent solution into the tube or ampoule, as stated in the following table:

Table 1. Sample test and reagent solutions for various digestion vessels

Digestion Vessel	Contoh uji (mL)	*Digestion solution* (mL)	Larutan pereaksi asam sulfat (mL)	Total volume (mL)
Tabung kultur				
16 x 100 mm	2,50	1,50	3,5	7,5
20 x 150 mm	5,00	3,00	7,0	15,0
25 x 150 mm	10,00	6,00	14,0	30,0
Standar Ampul:				
10 mL	2,50	1,50	3,5	7,5

Curve Calibrartion

Calibration The calibration curve is made in the following steps:

a) turn on the instrument and optimize the spectrophotometer test instrument according to the instructions for using the tool for COD testing. Set the wavelength at 600 nm or 420 nm;
b) measure the absorption of each working solution then record and plot the levels of COD; create a calibration curve from the data above and determine the equation for the straight line; b) if the linear regeneration correlation coefficient (r) <0.995, check the condition of the tool and repeat steps a) to c) until the coefficient r ≥ 0.995 is obtained. Measurement of the test sample
   For COD test samples 100 mg / L up to 900 mg / L a) cool the refluxed sample slowly to room temperature to prevent the formation of sediment. If necessary, occasionally open the sample cap when cooling to prevent gas pressure; b) let the suspension settle and make sure the part to be measured is really clear;
c) measure the absorption of the test sample at a predetermined wavelength (600 nm); d) calculate COD levels based on the linear equation of the calibration curve; e) do a duplo analysis. - For samples of COD less than or equal to 90 mg / L a) cool the refluxed sample slowly to room temperature to prevent the formation of sediment. If necessary, occasionally open the sample cap when cooling to prevent gas pressure; b) let the suspension settle and make sure the part to be measured is really clear; c) use water reagent as reference solution; d) measure the absorption of the test sample at a predetermined wavelength (420 nm); e) calculate COD levels based on the linear equation of the calibration curve; f) do a duplo analysis.

III. RESULTS AND DISCUSSION

In this study, the COD method validation refers to SNI 06-6898.2-2019. The sample used was sago waste water. Preparation of test samples by washing 16x100mm size culture tubes using 20% H_2SO_4. Preservation of the test samples using concentrated H_2SO_4 until the pH is less than 2, then stored in a cooler at 4˚C ± 2˚C with a storage time of 1 week.

Volume 03, Number 02, September 2020, Page 35-38
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Validation Results of Cod Analysis Method in Wastewater Using a Uv-Vis Spectrophotometer

A. Linearity

The result of the determination of the KHP (Potassium Hydrogen Phthalate) calibration curve is a linear line equation that can be used to calculate COD levels in wastewater samples. The linear regression line equation illustrates the relationship between the KHP concentration and the uptake of the KHP reaction compound with its reagents. The determination of the calibration curve in this study used 5 series of concentrations, namely 100 mg / L, 200 mg / L, 300 mg / L, 400 mg / L, 500 mg / L with 2 repetitions each. The wavelength used for absorption is 600nm. The results of the KHP standard curve determination are presented in table II.

Table 2. Result of Determination of KHP Calibration Curve to Determine

KHP concentration (mg / L)	Repetition 1	Repetition 2
100	0.045	0.041
200	0.096	0.085
300	0.128	0.123
400	0.171	0.174
500	0.213	0.205
r	0.998	0.998
Linear Regression Line Equations	y = 0.0004x +0.0073 R2 = 0.9964	y = 0.0004 + 0.0005 R2 = 0.996

The calibration curve has a good correlation coefficient (r) with a value of 0.998 each. This shows that the calibration curve is linear because r> 0.995 is in accordance with SNI 06-6898.2-2009. The value of r that approaches 1 indicates a relationship between concentration (x) and response (y) which is interpreted as linearity.

B. Accuracy / Precision

Determination of the precision value is done in 7 repetitions. precision is determined based on the standard deviation (SD). Based on the test results, it can be seen that the UV-VIS spectrophotometric method used for determining COD levels has a precision of 1.82% <2%. Presented in table III.

Table 3. COD Level Precision

No. Sample	COD levels (mg / L)	Average	SD	% RSD
1	146.75	147.11	2.67	1.82
2	151.75			
3	146.75			
4	149.25			
5	144.25			
6	144.25			
7	146.75			

C. Accuracy (Accuracy Test)

Accuracy is used to show the closeness of the analysis results to the actual analyte content. Accuracy in this validation is done by using recovery technique, namely the use of spiking against standard standards. The results of the linear regression equation for the calibration curve are y = 0.0004x + 0.0051 with a value of r = 0.999. Following the recovery results are presented in table IV.

Table 4. COD accuracy test results

Sample	% Recovery
1	96.39
2	98.06
3	99.66
4	98.03
5	96.33
6	99.65
7	99.66
Average	98.25

Accuracy is expressed as a percentage of recovery (% recovery). The test results showed that the average% recovery in COD levels gave good results and met the accuracy test requirements of 98.25%. The% recovery result is said to meet the requirements if it shows a percentage value between 85% -115%.

D. Detection Limit and Quantitation Limit Test (LOD and LOQ)

The determination of LOD and LOQ in this study was carried out by making a blank for 11 replications and a sample of 5 replications. Based on the results of LOD and LOQ measurements obtained, respectively, are 12.27 mg / L and 25.61 mg / L. The results of LOD and LOQ show that the sensitivity of the method is quite good.

IV. CONCLUSION

Based on the research results, it can be concluded that the method SNI 06-6898.2-2009 has good validation results including the r results obtained from the calibration curve equation of 0.998, a precision of 1.82%, an accuracy of 98.25% and LOD and LOQ of 12.27 mg / L and 25, 61 mg/L.

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Volume 03, Number 02, September 2020, Page 35-38
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