IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

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To cite this article: R T Rosmalina *et al* 2023 *IOP Conf. Ser.: Earth Environ. Sci.* **1201** 012046

Application of PeCOD and dichromate methods for the analysis of chemical oxygen demand (COD) in the wastewater sample

R T Rosmalina[1,2,*], D R Wulan[1], Widyarani[1], U Hamidah[1], Hidayat[1] and S Azman[2,*]

[1] Research Center for Environmental and Clean Technology, National Research and Innovation Agency, Kawasan Puspiptek Gedung 820, Tangerang Selatan 15314, Indonesia
[2] Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
*E-mail: tinarosmalina@yahoo.com; shamila@utm.my

Abstract. Chemical oxygen demand (COD) is one of the critical environmental parameters in determining the organic matter in water matrices. The conventional dichromate method employs hazardous reagents and heat reflux. In order to reduce hazardous waste, several alternative methods have been proposed to replace the dichromate. The photoelectrochemical COD (PeCOD) method has become a promising one for being less time-consuming, environmentally friendly, and more reliable. To ensure the result, a comparison between PeCOD and dichromate methods should be conducted. In this study, we analyzed the technical features of the PeCOD method, especially for the accuracy in measuring certified reference material (CRM), and identify the advantages and disadvantages of this method. Afterward, we applied both PeCOD and dichromate methods to analyze tofu processing wastewater as a representative of environmental samples. The result showed that PeCOD gave a recovery of 113.1±4.8% whereas the dichromate method gave a recovery of 98.4±1.7%, which indicates that the PeCOD method had lower accuracy than the dichromate method. Meanwhile, the COD concentration of tofu processing wastewater using PeCOD and dichromate methods was 11516±669 mg/L and 9109±680 mg/L, respectively. This difference might be due to overestimation by the PeCOD method, the complex matrix of the wastewater, and chloride interference.
Keywords: photoelectrochemical COD (PeCOD); dichromate method; accuracy; water sample; tofu processing wastewater

1. Introduction

Organic compounds are present in the majority of domestic and industrial wastewater effluents. In the streams where the effluents are discharged, these substances might adversely affect oxygen depletion (or demand), even at low concentrations [1]. The primary cause of this oxygen demand is the oxidative biodegradation of organic compounds by naturally occurring microbes that use the organic compounds as a source of food. While oxygen is absorbed and reduced to water, the organic substance is oxidized to carbon dioxide (CO_2). Almost all facilities that treat domestic wastewater must check the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of their treated effluents regularly.

In the sanitary and environmental fields, COD analysis is frequently used to determine the amount of organic matter in natural waters and wastewater. COD is the amount of oxygen (O_2) equivalents used when a strong oxidant (like potassium dichromate) breaks down organic matter chemically. It has a direct relation to the level of organic pollution in a water or wastewater sample [2,3].

Several methods have been widely used for COD analysis in water samples, for instance, the permanganate method and dichromate method which have been developed since the early 1950s [3]. The United States of America and Taiwan adopt the dichromate method as the standard method, while Japan adopts the permanganate method [4]. Compared to permanganate method, the dichromate method has a higher detection limit and reduces chloride ion interference owing to the stronger oxidant and the longer digestion time [5]. Therefore, the dichromate method is more quantitative in representing organic matter than the permanganate method. However, both of these methods have several disadvantages, i.e., hazardous chemical usage, time-consuming, and facing chloride interference. The photoelectrochemical COD (PeCOD) method, which employs a photocatalytic oxidation approach with titanium oxide (TiO_2) as a photocatalyst, has been introduced as a new technology since 2004 [6].

According to the Indonesian national standard (SNI 6989.73-2019) for dichromate method [7], a sample of liquid is reacted with a mixture of sulfuric and chromic acids (an oxidant) in the presence of silver sulfate (a catalyst for the oxidation of straight-chain hydrocarbons) and mercury sulfate for 2 h at 150°C. The Standard Method [8] suggests using the closed reflux-titrimetric method to reduce the large amount of hazardous waste. Mercury salt (for example, HgSO4) is usually added to reduce chloride ion interference by complexing the halide to mask the chloride ion [9]. This method is widely used because it provides high accuracy (94–104 %) and therefore is the standard method for COD analysis. Despite its wide application, the dichromate method has a few notable shortcomings: silver salts are expensive, digestion takes a while, and the most harmful interferents are chlorides, which are typically found in wastewater. These factors combine to form hazardous waste that contains residual silver and mercury in very acidic environments [2].

For this reason, it is desirable to search for environmentally friendly analytical methods that can yield accurate results, as recognized by the green analytical method. Photoelectrochemical COD (PeCOD) is a new technology that measures soluble COD in various water samples [6]. PeCOD was developed as a rapid, easy-to-use, and environmentally friendly technology that could replace dichromate as the standard method of measuring COD. PeCOD utilizes a calibrant solution prepared with sorbitol and an electrolyte prepared with lithium nitrate [10]. Used in sample preparation, this chemical is safe and can provide an accurate COD result in less than 15 minutes.

Even though the PeCOD method has advantages for COD analysis compared to the dichromate method, the data of the application on wastewater samples is still limited [9]. It is necessary to evaluate PeCOD application on tofu processing wastewater samples. In this study, COD analysis of the samples using PeCOD and dichromate methods was evaluated in order to compare their performance and identify the advantages and disadvantages of each method.

2. Material and methods

2.1. Materials

2.1.1. Certified reference material. The certified reference material (CRM) traceable to BAM (Germany) used in this study was obtained from Maja Bintang Indonesia. The CRM was a sorbitol solution with a COD concentration of 1200 mg/L. The CRM was stored at 4 °C until use. Due to the analysis range of the methods used in this study, the CRM was diluted with MilliQ water before analysis to obtain a concentration of 240 mg COD/L.

2.1.2. Wastewater sample. The wastewater sample was collected from a tofu processing factory in Central Java, Indonesia, and stored at 4 °C until use. Before the analysis with both methods, the sample was filtered using a 50 µM polyethylene (PE) syringe filter and diluted 80 times.

2.1.3. Chemicals. Potassium dichromate, mercury sulfate, sulfuric acid, silver sulfate, 10-phenanthrolin monohydrate, ferro ammonium sulfate (FAS), and potassium hydrogen phthalate were of analytical

IOP Conf. Series: Earth and Environmental Science 1201 (2023) 012046 doi:10.1088/1755-1315/1201/1/012046

grade and obtained from Merck. Electrolytes (lithium nitrate solution) was obtained from Maja Bintang Indonesia.

2.2. Dichromate method

The sample, CRM, or blank (5 mL) was added into a digestion tube (20 mm diameter), then 3 mL digestion solution and 7 mL sulfuric acid reagent solution were subsequently added to a total volume of 15 mL. The tubes were gently shaken until homogenous. The tubes were digested in a pre-heated heating block at 150 °C for 2 hours. After the digestion, the tubes were let cool to room temperature. The digestion mixtures were quantitatively transferred into Erlenmeyer flasks for titration. The samples were titrated with standard FAS solution using a ferroin indicator until there was a clear color change from green-blue to reddish-brown The difference between the initial and remaining oxidant concentrations in the sample (titration volume difference between sample and blank) was used to calculate the COD concentration [7,8].

2.3. PeCOD method

The analysis was performed using a MANTECH L50 PeCOD analyzer and yellow range electrolyte suitable for COD concentration of 200–750 mg/L [10].

The electrolyte and calibration solution were mixed at the appropriate ratio for the selected range. The PeCOD analyzer was primed with the blank and calibration solution. Calibration was performed to get the target value ± 5%. To perform the analysis, the CRM or wastewater sample was mixed at the appropriate ratio for the selected range and run on the analyzer.

2.4. Data analysis

To determine the accuracy and precision of the analysis, both dichromate and PeCOD methods were applied in ten replicates to measure COD concentration in the CRM. Afterward, the tofu processing wastewater sample was analyzed in six replicates.

Data from multiple measurements were calculated by descriptive statistics. Recovery of CRM was calculated using the following equation:

$$\text{Recovery}(\%)=\frac{\text{Measured concentration}}{240}\times 100\%$$

3. Results and discussion

3.1. Accuracy and precision

The accuracy and precision of PeCOD and dichromate methods were evaluated by measuring CRM with a COD concentration of 240 mg/L. The results can be seen in Table 1.

Table 1. Concentration and CRM recovery of PeCOD and dichromate methods (n=10).

	Concentration (mg/L)		Recovery (%)	
	PeCOD	**Dichromate**	**PeCOD**	**Dichromate**
Average	271.5	236.0	113.1	98.4
Standard deviation	11.5	4.1	4.8	1.7
Relative standard deviation (%)	4.2	1.7	4.2	1.7

Based on Table 1, the COD concentration of the CRM using PeCOD and dichromate methods was 271.5±11.5 mg/L and 236.0±4.1 mg/L, respectively. These are equivalent to recoveries of 113.1±4.8% (PeCOD) and 98.4±1.7% (dichromate). The results show that the accuracy of the PeCOD method was still lower than the dichromate. Furthermore, the PeCOD overestimated the COD concentration by an average of 13%. In terms of precision, the relative standard deviation of PeCOD was 4.2%, which was lower than AOAC's expected precision [11] for concentration of 100 ppm (5.3%), but still higher than the expected precision for concentration of 0.1% (3.7%).

3.2. Sample measurement

The results of the COD measurement of tofu processing wastewater are shown in Figure 1.

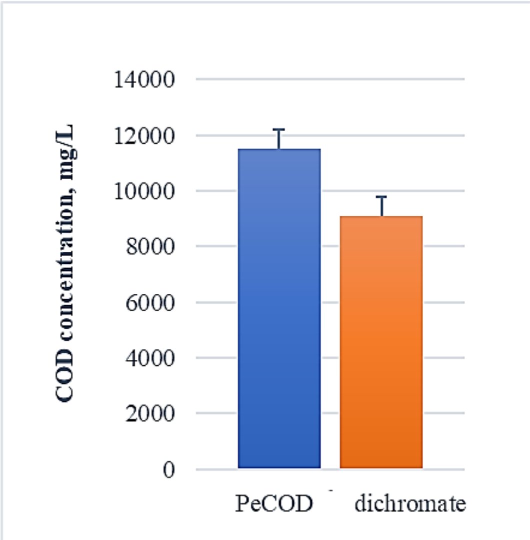

Figure 1. COD measurement performance using PeCOD and dichromate methods (n=6).

Based on Figure 1, the COD concentration of tofu processing wastewater using PeCOD and dichromate methods was 11516±669 mg/L and 9109±680 mg/L, respectively. Similar to CRM measurement, the result from PeCOD was higher than the dichromate method. This condition might occur on samples that have a large amount of organic matter in a complex matrix such as wastewater. Titanium oxide (oxidation potential of 3.2 V) is a stronger oxidant than potassium dichromate (1.6 V), therefore, it might oxidize complex organic matter more thoroughly [12]. The PeCOD method also did not employ measures to remove chloride. Interferences from chloride might occur in high-salinity water and wastewater samples such as tofu wastewater [13].

Despite these drawbacks, PeCOD has the advantages of being less time-consuming and practical in application [9]. Further studies should be conducted on factors that interfere with COD measurement using this method. Chloride removal methods using low-cost and non-toxic chemicals, such as bismuth-based adsorbent [14], should be explored. Alternatively, correction factors can be applied for samples containing high concentrations of chloride [15].

4. Conclusion

The result shows that PeCOD gave a recovery of 113.1±4.8%, whereas the dichromate method gave a recovery of 98.4±1.7%. From this result, the dichromate method has a higher accuracy than the PeCOD method. The COD measurement on real wastewater sample (tofu processing wastewater) using both methods show the COD concentration from the PeCOD method was 11516±669 mg/L, higher than 9109±680 mg/L from the dichromate method. This difference might be due to overestimation by the PeCOD method, the complex matrix of the wastewater, and chloride interference. Even though the PeCOD can be used for rapid and accurate COD quantification, the application on high concentration of organic matter in complex matrices should be studied further to ensure the alternative method of COD determination in environmental samples.

Acknowledgment
The authors would like to thank for the facilities, scientific, and technical support from Advanced Characterization Laboratories Bandung, National Research and Innovation Agency E- Layanan Sains. This work was conducted as a part of Universiti Teknologi Malaysia (UTM) and National Research and Innovation (BRIN), Degree by Research Program collaborative research grant vot R.J130000.7351.4B734.

Author contributions
RTR contributed in design experiment, methodology, writing-original draft. DRW contributed in experiment and data evaluation. W contributed in data evaluation, formal analysis, writing-reviewing and editing. UH and H contributed in experiment. SA contributed in supervision. All authors read and approved the final paper.

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