Voltammetric method for chemical oxygen demand in a dairy wastewater using homemade minimal instrumentation

Javier Ernesto Vilasó Cadre[a,*], Daniel Benítez Fernández[b], Héctor Rodríguez de la Rosa[c], María de los Ángeles Arada Pérez[d]

[a] Institute of Metallurgy, Universidad Autónoma de San Luis Potosí. San Luis Potosí, Mexico.
[b]Department of Research and Postgraduate in Foods, Universidad de Sonora. Sonora, Mexico.
[c]Lomas de San Luis International Hospital, Medical Research and Development, San Luis Potosí, Mexico.
[d]Chemistry Department, Faculty of Natural and Exact Sciences, Universidad de Oriente. Santiago de Cuba, Cuba.

Método voltamétrico para la demanda química de oxígeno en aguas residuales de lácteos utilizando instrumentación mínima de fabricación casera

Mètode voltamètric per a la demanda química d'oxigen en aigües residuals làcties utilitzant una instrumentació mínima casolana

RECEIVED: 8 MARCH 2022; ACCEPTED: 2 NOVEMBER 2022 ; DOI: https://doi.org/10.55815/413408

ABSTRACT

This paper presents a voltammetric method for the Chemical Oxygen Demand (COD) quantification in a dairy wastewater using homemade minimal electrochemical instrumentation. The working electrode was a carbon microdisc, the auxiliary electrode was a carbon rod, and a silver electrode was used as reference. A low-cost non-commercial potentiostat was employed. The linear working range was 1-20 g/L. Repeatability was evaluated on 10 sample quantifications, the coefficient of variation was 3.6%, lower than that obtained for the reference spectrophotometric method (8.2%). The voltammetric method did not require treatment of the sample. The trueness was evaluated by comparing the voltammetric results with the spectrophotometric method. Mean COD of 10 quantifications using low-cost voltammetry was 10.2 g/L, whereas for the spectrophotometric method it was 11.0 g/L. A Paired Sample t-Test did not show statistically significant differences between both. The detection limit was 0.6 g/L and the quantification limit was 1.8 g/L. Both are acceptable for the sample in which there is a high organic content.

Keywords: COD, dairy wastewater, low-cost, voltammetry.

RESUMEN

Este artículo presenta un método voltamperométrico para la cuantificación de la Demanda Química de Oxígeno (DQO) en aguas residuales de una lechería utilizando instrumentación electroquímica mínima casera. El electrodo de trabajo fue un microdisco de carbono, el electrodo auxiliar fue una barra de carbono y se utilizó como referencia un electrodo de plata. Se empleó un potenciostato no comercial de bajo costo. El rango de trabajo lineal fue de 1-20 g/L. La repetibilidad se evaluó en 10 cuantificaciones de muestra, el coeficiente de variación fue de 3,6%, inferior al obtenido por el método espectrofotométrico de referencia (8,2%). El método voltamétrico no requirió tratamiento de la muestra. La veracidad se evaluó comparando los resultados voltamperométricos con el método espectrofotométrico. La DQO media de 10 cuantificaciones por voltamperometría de bajo coste fue de 10,2 g/L, mientras que por el método espectrofotométrico fue de 11,0 g/L. Una prueba t para muestras pareadas no mostró diferencias estadísticamente significativas entre ambos. El límite de detección fue de 0,6 g/L y el límite de cuantificación fue de 1,8 g/L. Ambos son aceptables para la muestra, en la que existe un alto contenido orgánico.

Paraules clau: DQO, aguas residuales de lácteos, bajo coste, voltamperometría

***Corresponding author: jvilasocadre@gmail.com**

RESUM

Aquest article presenta un mètode voltamètric per a la quantificació de la demanda química d'oxigen (DQO) en aigües residuals làctiques mitjançant instrumentació electroquímica mínima casolana. L'elèctrode de treball era un microdisc de carboni, l'elèctrode auxiliar era una vareta de carboni i es va utilitzar un elèctrode de plata com a referència. Es va utilitzar un potentiòstat no comercial de baix cost. El rang de treball lineal va ser d'1-20 g/L. Es va avaluar la repetibilitat en 10 quantificacions de mostres, el coeficient de variació va ser del 3,6%, inferior al obtingut pel mètode espectrofotomètric de referència (8,2%). El mètode voltamètric no va requerir tractament de la mostra. La veracitat es va avaluar comparant els resultats voltamètrics amb el mètode espectrofotomètric. El DQO mitjà de 10 quantificacions utilitzant voltametria de baix cost va ser de 10, 2 g/L, mentre que per al mètode espectrofotomètric va ser d'11, 0 g/L. Una prova t de mostra aparellada no va mostrar diferències estadísticament significatives entre ambdues. El límit de detecció era de 0,6 g/L i el límit de quantificació era d'1,8 g/L. Tots dos són acceptables per a la mostra en què hi ha un alt contingut orgànic.

Paraules clau: DQ, aigües residuals làctiques, baix cost, voltametria

INTRODUCTION

Chemical oxygen demand (COD) is defined as the amount of oxygen required, or equivalent, to chemically transform the oxidizable matter in the water. This is a parameter widely used to evaluate contamination in water and wastewater. It is frequently used as a measure of the organic pollutants because they are the most easily oxidized [1].

The common methods for quantifying COD use a strong oxidizing agent such as potassium dichromate, in addition to other reagents that participate in the process such as silver and mercury salts, and sulfuric acid. The oxidation can be carried out at open or closed reflux, and COD can be quantified using volumetry or UV-Visible molecular absorption spectrophotometry [2]. However, these methods have several drawbacks: they are very laborious techniques and they use expensive and toxic reagents.

Oxidizable matter in a liquid sample can also be transformed electrochemically, being possible to stablish a chemical analysis method, such as voltammetry. This method is based on the measurement of the current intensity which flows through an electrolytic cell by imposing a variable potential difference [3].

Several authors have reported the development of non-commercial voltammetric methods. All research has been focused on metals and specific organic analytes. Montoya et al. [4] presented the construction of a homemade potentiostat and its application to the quantification of cadmium, copper, lead, nickel, zinc, and other trace elements in water. They observed the expected voltammetric pattern and good linearity of the calibration curves. Ghoreishizadeh et al. [5] presented a nano-sensor and a circuit construction for anti-cancer drug detection. Results demonstrated the possibility of quantifying drugs with the non-commercial instrument based on cyclic digital scan. Bukkawar et al. [6] reported a low-cost portable potentiostat for biosensing applications. More minimalist voltammetric instrumentations have been reported by other authors. Khan and Khanam [7] showed a simple circuit for the polarographic study of cadmium complexes with some L-amino acids and vitamin C. There are not reports about using homemade voltammetric instrumentation for COD quantification.

In this paper, a homemade minimal potentiostat was used for COD quantification in a dairy wastewater. The novelty lies in the demonstration of using a basic electrical circuit to determine this quality parameter truthfully and precisely.

MATERIALS AND METHODS

Experimental sample and reagents

The experimental sample was a residual whey from the production of cheese and yogurt. All reagents were provided by Sigma-Aldrich and deionized water was used.

Voltammetric COD quantification

A homemade minimal potentiostat reported by Vilasó et al. [8] was used for the voltammetric COD quantification in a dairy wastewater. Figure 1 shows the circuit design.

A carbon microdisc was used as the working electrode and a bar of the same material was used as the auxiliary electrode. The reference electrode was a silver wire. 1 mol/L KNO_3 was used as the supporting electrolyte. Anodic potential staircase scans were performed from 0 to 1900 mV to record the voltammograms [9]. A calibration curve of lactose was prepared based on the fact that this carbohydrate is the main organic component of whey [10].

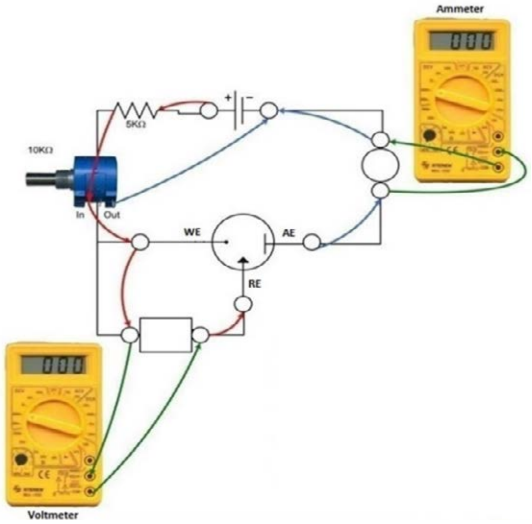

Figure 1. *Circuit design of the homemade minimal potentiostat used for COD quantification in a dairy wastewater [8].*

Linearity

Voltammograms were recorded at lactose concentrations: 1; 5; 10; 15 and 20 g/L. Diffusion current was plotted as a function of concentration. Three curves were obtained by linear regression [11].

Trueness and repeatability

Trueness of voltammetry was evaluated considering the spectrophotometric method as a reference. A Paired Sample t-Test was conducted from 10 COD quantifications using both methods. For the evaluation of repeatability, the same 10 quantifications were used for the calculation of the coefficient of variation [11].

Limits of detection and quantification

The limit of Detection (LOD) was calculated from the calibration curve using the equation 1, whereas the limit of Quantification (LOQ) was calculated by the equation 2 [12].

$$\mathrm{LOD} = 3(\sigma/\mathrm{S}) \qquad \text{(Eq. 1)}$$

$$\mathrm{LOQ} = 10(\sigma/\mathrm{S}) \qquad \text{(Eq. 2)}$$

Where LOD is the Limit of Detection, LOQ is the Limit of Quantification, σ is the standard deviation of the intercept, S is the slope.

Reference COD quantification

COD was quantified using the reference spectrophotometric method with closed reflux. $K_2Cr_2O_7/HgSO_4$ was used as the oxidant digester solution. The catalyst solution was 10 g/L Ag_2SO_4/ H_2SO_4. A calibration curve of potassium hydrogen phthalate was prepared. The volume of standard solution corresponding to each concentration of the curve was mixed with 2 mL of the catalyst solution and 1 mL of the digester solution, then it was filled up to 5 mL with water. The standards were prepared in COD capped test tubes. After homogenizing, they were heated at 150°C for 2 h in a Hach COD reactor. The dairy wastewater samples received the same treatment as the calibration curve standards. 1 mL of sample was taken for analysis after making a 1/100 dilution. After the digestion process, the test tubes were cooled and the absorbance was measured at 600 nm [2].

RESULTS

Linearity

Figure 2 presents the calibration curve for the voltammetric quantification of COD in a dairy wastewater. Table 1 shows the descriptive statistical information about regression.

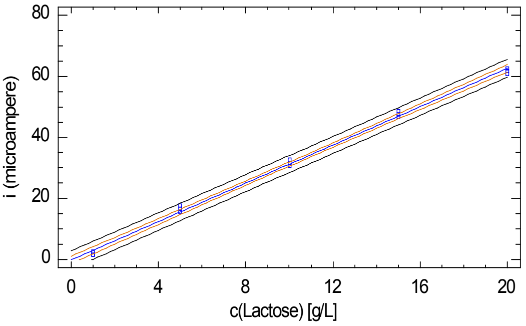

Figure 2. *Calibration curve for the voltammetric method for COD quantification in a dairy wastewater.*

Table 1. *Descriptive statistical information about the calibration curve for the voltammetric method for COD quantification in a dairy wastewater.*

Correlation coefficient (r)	0.9985
Determination coefficient (R^2)	0.9970
Determination coefficient adjusted (($R^2_{adj.}$)	0.9968
Residue's average	0.965376
Slope (S)	3.12709
Intercept	0.000306181
Slope error	0.0473126
Intercept error (σ)	0.579845

Trueness and repeatability

Table 2 shows the COD results obtained using voltammetry and the reference spectrophotometric method. The statistic values of the Paired Sample t-Test are shown too.

Table 2. *COD results obtained by voltammetry and spectrophotometry for a dairy wastewater. Paired Sample t-Test statistics.*

	COD (g/L)	
Quantification	***Voltammetry***	***Spectrophotometry***
1	10.4	11.7
2	10.4	10.8
3	9.8	11.1
4	10.4	9.2
5	10.4	9.9
6	9.8	11.6
7	10.1	12.3
8	9.8	11.1
9	9.8	11.1
10	10.8	11.4
Mean	10.2	11.0
S.D.	0.3630	0.9036
C.V.	3.5	8.2
Paired Sample T-Test		
t-Student = -2.5726	***p-value*** = 0.0300591	***Significance level*** = 0.01

S.D.: Standard deviation, C.V.: Coefficient of variation

Detection and quantification limits

Table 3 shows the detection and quantification limits for the COD voltammetric method using homemade low-cost electrochemical instrumentation.

Table 3. *Limits of detection and quantification for the voltammetric method for COD quantification in a dairy wastewater.*

Limit	COD (g/L)
Detection	0.6
Quantification	1.8

DISCUSSION

Figure 2 shows that the current increases as the concentration does. An adequate linearity of the data is observed with a low intercept value. That is confirmed by the parameters shown in the Table 1. The correlation coefficient (r) indicates a strong linear dependence between current and concentration. The determination coefficient (R^2) shows that the mathematical model generated by regression explains the 99.70 % of the variability of the method. The determination coefficient adjusted for degrees of freedom ($R^2_{adj.}$) is more suitable for comparisons. This coefficient (0.9968) obtained with low-cost instrumentation and a graphite working electrode is in correspondence with the range of 0.9890 to 0.9940 reported by Hamdy et al. [13] for a more expensive electrochemical method based on an electrodeposited nano-copper film electrode. The residues (0.965376) demonstrate a low deviation between estimated and experimental values. Equation 3 shows the mathematical expression corresponding to the COD quantification curve.

$$i = 3.12709 \cdot COD + 0.000306181 \qquad \textit{(Eq. 3)}$$

For evaluating trueness, a Paired Sample t-Test was carried out with respect to the reference spectrophotometric method. Because the p-value (0.0300591) is greater than 0.01, the null hypothesis about no differences cannot be rejected for the confidence level of 99%, therefore, the results obtained by the spectrophotometric and voltammetric methods are consistent, so this last one is true.

The repeatability of the voltammetric method is adequate considering that the coefficient of variation is less than 4 % reported for this kind [14]. The coefficient of variation is also lower than that obtained for the spectrophotometric method. This may be associated with oxidative treatment of the sample when using spectrophotometry, which is not necessary for voltammetry. During closed reflux oxidation, random errors such as incomplete oxidation and the effect of interferents can occur [2].

The detection of minimum COD by this method is limited by the staircase scan used, which is an adaptation of the linear scan for this instrumentation. The linear scan is not highly sensitive like the differential or square wave scans; however, the limits of detection and quantification are adequate for the wastewater analyzed because it has a high organic content.

CONCLUSIONS

The homemade minimal instrumentation potentiostat allows the linear, true and low dispersed COD voltammetric quantification in a dairy wastewater using graphite electrodes and staircase potential scan. The voltammetric method has less errors than spectrophotometry because oxidative treatment of the sample is not necessary. The limits of detection and quantification are appropriate for the sample due to the high organic content.

REFERENCES

1. Li, J., Luo, G., He, L., Xu, J., Lyu, J. (2018). Analytical Approaches for Determining Chemical Oxygen Demand in Water Bodies: A Review. Crit. Rev. Anal. Chem., 48(1), 47-65. https://doi.org/10.1080/10408347.2017.1370670.
2. Rice, E.W., Baird, R.B., Eaton, A.D. (2017). Standard Methods for the Examination of Water and Wastewater. 23rd Ed. American Public Health Association, Washington, 1368 pp. ISBN: 978-0875530475.
3. Aoki, K.J., Chen, J. (2018). Tips of Voltammetry. In: Voltammetry, Wendy, N.M. (Editor). IntechOpen, London, 19 pp. https://doi.org/10.5772/intechopen.81341.
4. Montoya, E., Baltuano, O., Montoya, H., Mendoza, M., Hernandez, Y. (2002). A low-cost PC-based voltammetric analyzer for determination of cadmium, copper, lead, nickel, zinc and other trace elements in water. Informe Científico Tecnológico IPEN, 2, 105-107. ISSN: 1684-1662.
5. Ghoreishizadeh, S.S., Baj-Rossi, C., Carrara, S., De Micheli, G. (2011). Nano-Sensor and Circuit Design for Anti-Cancer Drug Detection. IEEE/NIH Life Science Systems and Applications Workshop (LiSSA), 28-33. https://doi.org/10.1109/LISSA.2011.5754147.
6. Bukkawar, S., Sarwade, N., Panse, M.S., Muthurajan, H. (2017). Design and Development of Portable Potentiostat for Advanced Research in Electrochemical Biosensing. IEEE International Conference on Power, Control, Signals and Instrumentation Engineering (ICPCSI), 2531- 2535. https://doi.org/10.1109/ICPCSI.2017.8392173.
7. Khan, F., Khanam, A. (2008). Study of complexes of cadmium with some L-amino acids and vitamin-C by voltammetric technique. Ecletica Quim. J., 33(2), 29-36. https://doi.org/10.1590/S0100-46702008000200004.
8. Vilasó, J.E., Arada, M.A., Baeza, J.A., Céspedes, A. (2016). Construction and Metrological Characterization of a Minimal Instrumentation Micropolarograph. Port. Electrochim. Acta, 34(5), 309-320. https://doi.org/ 10.4152/pea.201605309.

9. Vilasó, J.E., Arada, M.A., Arce, J., M.A., Baeza, J.A. (2020). Study of the potential sweeps in the manual staircase voltammetry. Rev. Cubana Quím., 32(2), 287-298. ISSN: 2224-5421.
10. Durham, R., Hourigan, J.A. (2007) Waste management and co-product recovery in dairy processing. In: Handbook of Waste Management and Co-Product Recovery in Food Processing, Waldron, K. (Editor). Woodhead Publishing Limited, Sawston, 55 pp. https://doi.org/10.1533/9781845692520.4.332.
11. Oficina Nacional de Normalización (2010). Guía para la Validación de Métodos Químicos de Ensayo, NC-TS-368-2010. La Habana.
12. Segül, S. (2016). Comparing determination methods of detection and quantification limits for aflatoxin analysis in hazelnut. J. Food Drug Anal., 24(1):56-62. https://doi.org/10.1016/j.jfda.2015.04.009.
13. Hamdy, H., Ibrahim, B., Hesham, A., Esmat, E., Ali, A. (2018). Low-cost chemical oxygen demand sensor based on electrodeposited nano-copper film. Arab. J. Chem., 11(2), 171-180. https://doi.org/10.1016/j.arabjc.2015.07.001.
14. Skoog, D.A., Holler, F.J., Crouch, S.R. (2008). Principles of Instrumental Analysis. 6th Ed. Cengage Learning. Boston, 1063 pp. ISBN: 978-0495012016.