

A single-chamber microbial fuel cell as an alternative biosensor for continuous and onsite determination of BOD in wastewater

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Abstract. The two main pollution parameters, BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand), are crucial factors in assessing water quality and pollution levels. Currently, COD can be measured using sensor devices, while BOD relies on the activity of microorganisms. Traditionally, the quantification of biologically oxidizable organic carbon involves measuring oxygen consumption over a five-day period, commonly known as the BOD₅ test. However, the BOD₅ test has several disadvantages, such as its time-consuming nature, unsuitability for process control, and the requirement for highly skilled samplers. It was hypothesized that the output of a single-chamber microbial fuel cell (SCMFC) with an air-cathode could serve as an alternative method for measuring BOD. To validate this hypothesis, this study conducted some experiments using the model of SCMFC. When artificial wastewater, utilizing sodium acetate as fuel, was employed, a strong linear correlation ($R^2 > 0.99$) between the total charge transferred and BOD₅ concentration was confirmed. Additionally, the linear relationship was also investigated for real domestic wastewater, resulting in a combined correlation with an R^2 value exceeding 0.98. Until now, research on biosensors (particularly SCMFC-based biosensors) in Viet Nam is still relatively new and has not been extensively conducted. The results of this study could provide a solid foundation for the development of continuous and onsite BOD sensors to monitor BOD concentrations in wastewater streams.

Keywords: BOD, single-chamber microbial fuel cell, voltage, biosensor, wastewater.

Classification numbers: 3.3.3, 3.4.2.

1. INTRODUCTION

Microbial Fuel Cells (MFCs) have been developed as an alternative sensor device for directly and continuously measuring BOD in wastewater [1]. The basic structure of an MFC consists of a pair of electrodes (cathode/anode) connected by an external resistor [2]. Bacteria with exoelectrogenic capabilities on the anode oxidize organic compounds in wastewater, transferring electrons to the cathode through an electric circuit [3, 4]. As a result, electrical energy is generated through microbial metabolism. Accordingly, the electrical output of an MFC can be correlated with biodegradable organic matter concentration, providing a basis for BOD quantification. Typically, the construction of MFCs includes two basic types: single-chamber and

two-chamber. For the two-chamber type, the anode chamber contains an anaerobic environment, while the cathode chamber contains an aerobic environment. The two chambers are separated by an ion-selective membrane such as Nafion [5, 6]. In the case of the single-chamber type, the cathode chamber is directly exposed to O_2 from the air (Figure 1). This is also one of the key advantages of the single-chamber MFC (SCMFC) over the double-chamber type, as it eliminates the need for air bubbling at the cathode, reducing energy consumption costs.

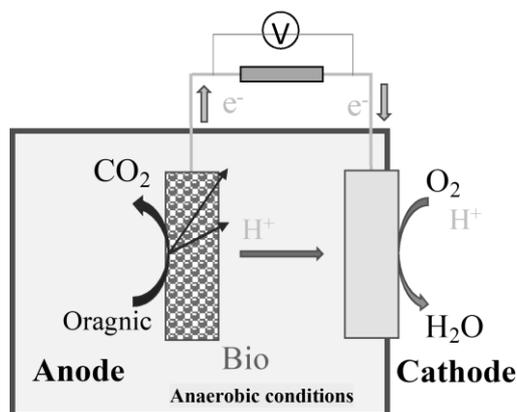


Figure 1. Schematic diagram of a Single Chamber Microbial Fuel Cell (SCMFC).

Forty years ago, Karube *et al.* [7] first proposed the use of Microbial Fuel Cells (MFCs) as BOD sensors, in which *Clostridium butyricum* bacteria were immobilized on the anode electrode. The operational results demonstrated a linear relationship between the generated current from the MFC and BOD concentration, confirming the feasibility of MFC-based BOD sensors. Subsequently, various types of MFC-based BOD sensors with different strains of microorganisms were cultured and experimentally investigated [8, 9]. Compared to conventional biological sensors, MFC-based biological sensors use directly measured current or voltage as output signals [10], making them more convenient for processing and displaying. Moreover, they can be designed and applied in remote areas due to their self-powering capability. Despite significant achievements in research, practical applications of MFC-based BOD sensors are limited due to their relatively long adaptation times and high-tech equipment requirements. In Viet Nam, research on biological sensors in general, and MFC-based biological sensors in particular, is still relatively novel and has not been extensively explored. Existing studies have mainly focused on microbial enrichment and fundamental electrochemical characteristics of MFCs, with limited application to environmental monitoring and biological BOD sensing [11, 12].

The BOD₅ test has been widely used to determine BOD in wastewater; however, its time-consuming and laboratory-dependent nature limits its applicability for continuous water quality control and operational management at wastewater treatment plants. BOD sensors based on MFC present an opportunity to liberate BOD parameter measurements from the confines of the laboratory. Moreover, rapid, accurate, and continuous BOD quantification has the potential to optimize wastewater treatment processes based on the input water quality and wastewater conditions throughout the operation. Therefore, applying a SCMFC model as BOD sensors serves as a foundational step in advancing research on biological sensors in water and wastewater treatment.

In this study, a series of experiments were performed utilizing the SCMFC model. Our primary research objectives were twofold: firstly, to establish a correlation between the total

charge and BOD₅ levels in artificial wastewater samples, and secondly, to validate the accuracy and reliability of the method by examining real wastewater samples.

2. MATERIALS AND METHODS

2.1. SCMFC reactor and operation

The SCMFC of this study was rectangular, with a total volume (V_{cell}) of 220 mL, resulting in a total anodic volume of 25 mL. As can be seen in Figure 2, the fuel cell consisted of an anode and an air-cathode, separated by a Nafion membrane with a working area of 5 cm². Both electrodes utilized carbon cloth (AA304ZS, Toyobo Co. Ltd, Japan) with an area of 8 cm² per electrode. The anode electrode was placed on one side of the cylinder (anode chamber) under anaerobic conditions and was connected via titanium wires. A small quantity of anaerobic sludge, obtained from a laboratory-scale up-flow anaerobic sludge blanket (UASB) reactor [13], was inoculated on the surface of the electrode, functioning as a bio-anode. The cathode electrode was prepared using the rolling method, as described in previous studies [14, 15]. It was placed on the open side of the plastic chamber, featuring a conductive oxygen gas diffusion layer (PTFE suspension with AC/PTFE mass ratios of six) facing the air, and an AC catalyst layer (1500 m²/g, Xinsen Carbon Co. Ltd., Fujian, China) facing the substrate medium. An external resistor was placed between the two electrodes to measure the current generated in the circuit by recording voltage using a digital multimeter (FlEpow; Levin Japan). Previous studies have highlighted the influence of external resistance on the SCMFC's performance [16]. Therefore, in this study, two specific resistance values were selected: 200 Ω for the enrichment period under continuous mode and 500 Ω for batch experiments, aiming to investigate the correlation between total charge and BOD₅ concentration.

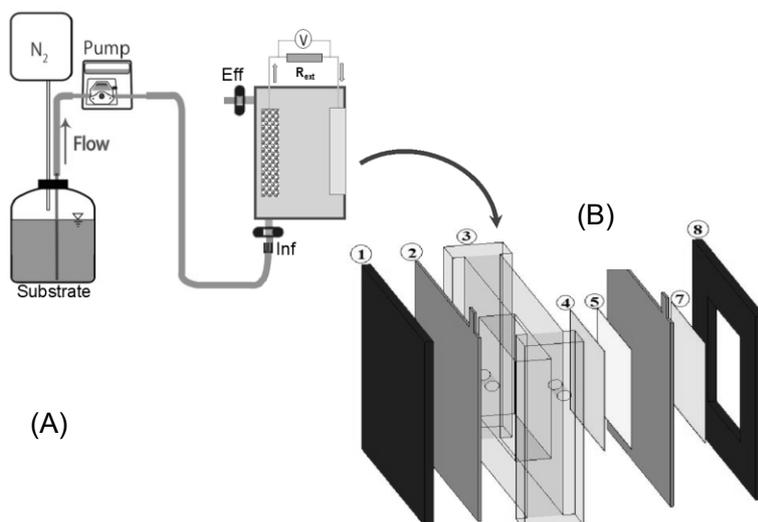


Figure 2. Schematic diagram of Single Chamber Microbial Fuel Cells used this study. (A) SCMFC (Influent tank, SCMFC model, R_{ext} external resistance). (B) Details of SCMFC configuration – 1, 3, 8: SCMFC body; 2: Carbon cloth (anode); 4: Nafion (ion-selection membrane); 5: Catalyst layer; 6: Carbon cloth (cathode); 7: Oxygen diffusion (PTFE).

The anode chamber was filled with the substrate medium and deoxidized through a nitrogen purge. The experiments were performed on synthetic wastewater with sodium acetate as a source

of BOD₅ and on domestic wastewater samples collected directly from residential areas in Ho Chi Minh City. The substrate medium's pH was adjusted to approximately 6.5-7.5 before entering the SCMFC using a phosphorus buffer. For the synthetic wastewater, in addition to sodium acetate as the main component, there were supplementary additions: (1) trace elements including FeSO₄·7H₂O (7 mg/L), CoCl₂·6H₂O (1.7 mg/L), ZnSO₄·7H₂O (1.5 mg/L), HBO₃ (0.6 mg/L), MnCl₂·4H₂O (4.2 mg/L), NiCl₂·4H₂O (0.4 mg/L), CuCl₂·2H₂O (0.27 mg/L), and Na₂MoO₄·2H₂O (0.25 mg/L); (2) minerals including MgCl₂·6H₂O (4.0 mg/L), CaCl₂·2H₂O (1.5 mg/L), and KCl (3.0 mg/L); and (3) ammonium NH₄⁺ (2.0 mg/L).

The SCMFC was conducted in two phases: enrichment and batch experiments. In the enrichment phase, acetate substrate (35.7 mM) was used under continuous mode to establish stable operation before conducting measurements in batch experiments. During the batch experiment phase, initial measurements for artificial wastewater were taken with varying amounts of sodium acetate, and then they were applied to two types of domestic wastewater. Each batch experiment was conducted at a specific BOD₅ value, and this process was repeated three times. Analysis of liquid samples at the beginning and end of each batch operation was performed, and BOD₅ and COD measurements were carried out following international standards (APHA 1999).

2.2. Analysis and calculations

The voltage measured was converted into current according to Ohm's law. Coulombs, expressed as current × time, were calculated by integrating the current over time from the start point of the experiment to the cutoff potential. Coulombic efficiency is defined as the ratio of actual coulombs of charge delivered to the anode to the total coulombs of charge generated, assuming that the total COD is being converted to biogenic electricity with a theoretical ratio of 4 mol of electrons/mol COD. The actual coulombs obtained were determined by integrating the current over time. Therefore, Eq. (1) was used to calculate the coulombic efficiency for the SCMFC operating in fed-batch mode, measured over time *t*.

$$CE = \frac{M \times \sum I \Delta t}{4 \times \Delta COD \times V_{an} \times F} \quad (1)$$

where *CE* is coulombic efficiency, *I* is the current (A), *t* is the time (s), *M* is the molecular weight of oxygen (32), *V_{an}* is the total anodic volume (L), *F* is the Faraday's constant (96485.3 C/mol-electrons), and *ΔCOD* (g/L) is the variation in COD during the experiment.

3. RESULTS AND DISCUSSION

3.1. Enrichment

The anode of the SCMFC was inoculated with diluted anaerobic sludge. The enrichment was sustained using artificial wastewater containing sodium acetate (35.7 mM), trace elements (1 mL/L), and minerals (0.5 mL/L) [17]. Figure 3 presents the variation in output voltage of the SCMFC over time under an external load of 200 Ω. The substrate medium was continuously supplied to the SCMFC at a rate of 0.224 mL/s to observe system performance from start-up to steady-state conditions. In the initial four days, an electric current was generated in the circuit, and the measured voltage increased gradually from 0.18 V to 0.28 V. However, starting from the fifth day, the output increased more rapidly and stabilized at the level of 0.6–0.65 V. This voltage evolution reflects enhanced electrochemical activity of the anodic biofilm, indicating that enrichment of electroactive bacteria was completed within approximately eight days.

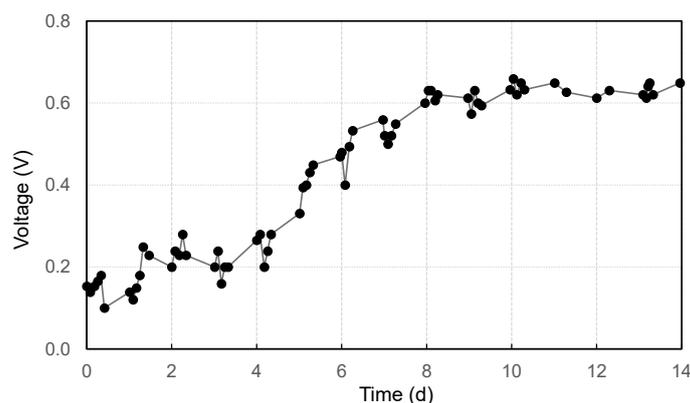


Figure 3. Various output voltages of the SCMFC over time when fed with sodium acetate solution in continuous mode.

3.2. Performance of batch experiments

After the completion of the enrichment process, the SCMFC operated in sequential batches to establish the correlation between the electrical charge across the circuit and the corresponding BOD_5 concentration. The artificial wastewater was carefully regulated, with sodium acetate as the main component, supplemented with minerals, trace elements, and a phosphorous buffer to maintain the pH within the model at approximately 6.5 - 7.5. Five different values of BOD_5 concentrations (81, 159, 318, 417, 636 mg/L) were used, with each BOD_5 value corresponding to one batch and each batch was repeated three times. After testing artificial wastewater samples, the SCMFC continued to be used for processing domestic wastewater with BOD_5 concentrations of 178 and 253 mg/L, under the same experimental conditions as the artificial samples. Considering the BOD_5 value used in the enrichment and the concentration dependence of the voltage in the cell [18], an external resistance of 500 Ω was chosen for batch experiments.

Initially, SCMFC was operated with a BOD_5 of 318 mg/L. The voltage reached its maximum immediately after filling up the substrate into the model and then gradually decreased due to fuel consumption. When the voltage dropped to approximately 0.1 V, it was observed that the voltage no longer decreased. Continuing to maintain this condition for an additional 24 hours showed no change in voltage. In the subsequent batches, for example, at BOD_5 concentrations of 159 and 477 mg/L, the measured voltage exhibited tendencies like those seen at a concentration of 318 mg/L. Therefore, 0.1 V serves as the baseline voltage without substrate, related to endogenous respiration. It may also function as the cutoff potential. However, when applied to real wastewater, the voltage dropped to a lower level, reaching a cutoff potential of 0.06 V.

3.2.1. Evaluation of measurements with artificial media samples and real wastewater samples.

Figure 4 shows the temporal variation in voltage corresponding to different concentrations of sodium acetate. The maximum voltage output appeared as near-instantaneous peaks upon sample insertion and gradually decreased to the established cutoff potential of 0.1 V. Within the range of low BOD_5 concentrations (<320 mg/L), the voltage demonstrated a proportional relationship with BOD_5 concentration. However, at higher BOD_5 levels, the voltage reached its maximum at almost a consistent value. These findings align with prior studies on SCMFC employing air-cathodes [16, 19, 20], while total charge was correlated with a BOD concentration of up to 520 mg/L in a two-chambered system [21]. The broader dynamic range observed for the

air-cathode SCMFC suggests that BOD sensor performance can be enhanced through appropriate cathode selection. Additionally, the correlation between maximum current output and BOD₅ concentration implies the potential for continuous, real-time BOD measurements *in situ*.

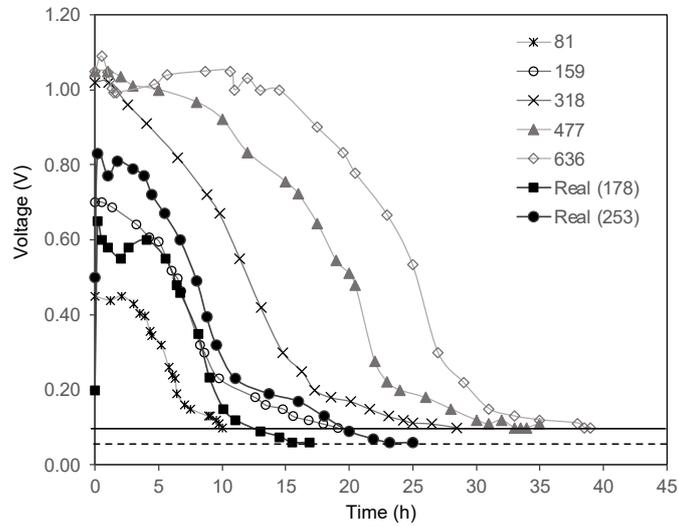


Figure 4. Voltage vs time curves for artificial wastewater (with different concentrations of sodium acetate) and domestic wastewater. Solid line: 0.1 V cutoff potential applied for artificial wastewater; Dashed line: 0.07 V cutoff potential applied for domestic wastewater.

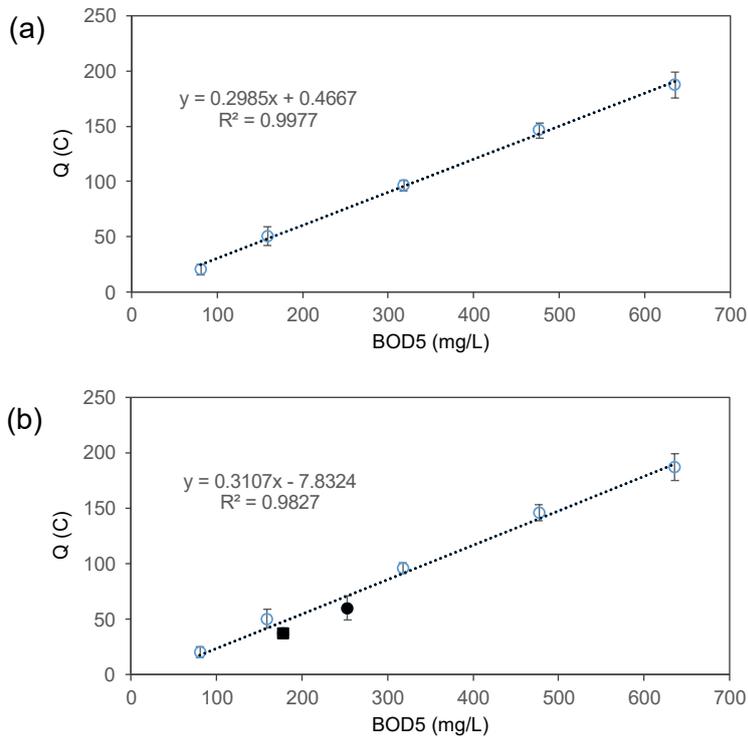


Figure 5. (a) Linear correlation between total charge value and BOD₅ concentration for artificial wastewater (with different amounts of sodium acetate); (b) Combined linear correlation between total charge value and BOD₅ concentration for artificial wastewater.

In Figure 5(a), a good linear correlation is observed between the calculated total charge values and the BOD₅ values of the artificial samples, with a coefficient of determination (R^2) exceeding 0.99. Despite a slight reduction in the output voltage for real wastewater compared to measurements derived from sodium acetate, employing a unified calibration approach for both artificial and real wastewater is recommended (Figure 5(b)). Notably, the R^2 values for the consolidated linear correlations consistently exceed 0.98, demonstrating the high precision and reliability of this analytical method. This outcome confirms that both wastewater types can be accurately assessed using a single calibration line, underscoring the robustness and applicability of the proposed method for environmental monitoring applications.

3.3.2. Coulombic efficiency

Achieving high coulombic efficiency is essential for the optimal operation of MFC-based biosensors, particularly in the presence of alternative electron acceptors such as nitrate and oxygen with higher redox potentials, which may reduce signal strength and biosensor performance. In this study, the utilization of artificial wastewater as a fuel in the small-volume SCMFC biosensor may yield the best performance in terms of response time and coulombic efficiency. Employing a nitrogen purge to deoxygenate the substrate was adopted as a strategy to limit dissolved oxygen (DO) in water [5, 22]. However, the coulombic efficiencies of this SCMFC were moderate, with values of 44.0 %, 42.8 %, 41.4 %, 41.2 %, and 40.1 % for BOD₅ concentrations ranging from 81 to 636 mg/L in artificial wastewater. For real wastewater, the coulombic efficiency was lower, reaching 36 % at an influent BOD₅ concentration of 178 mg/L. The observed lower efficiencies may be attributed to the entry of oxygen into the reactor, creating a competition between DO and the anode for the electrons released from the substrate. Notably, in systems with an air-cathode, substantial oxygen diffusion into the anode chamber is anticipated, even with a polymeric membrane like Nafion [23]. Furthermore, compared with previous studies, the initial concentration of substrates also impacts Coulombic efficiency [16, 19]. At lower BOD₅ concentration, shorter substrate consumption times may partially mitigate these effects. These findings suggest that future studies should explore aerobic respiration inhibitors to further enhance SCMFC-based biosensor performance.

The limitations of the traditional measurement method, which requires a five-day incubation period and skilled personnel, motivate the exploration of alternative approaches. Additionally, the two-hour setup time further limits its applicability for routine or on-site testing, particularly in remote locations. In this context, the SCMFC-based biosensor represents a promising alternative to the conventional BOD₅ test for rapid and accurate BOD monitoring in water treatment and regulatory applications. The stable anodic biofilm and the proportional relationship between substrate concentration and microbial metabolic activity support the feasibility of SCMFC-based BOD sensors. Evaluating the performance of the SCMFC based on a BOD sensor using varying concentrations of sodium acetate solution and real wastewater in this study demonstrated a strong linear correlation between BOD concentration and transferred charge (> 0.98), showcasing its applicability under specific conditions. Overall, this approach offers a more efficient and more timely alternative to conventional BOD₅ measurements, while acknowledging its current limitations.

4. CONCLUSIONS

This study demonstrated that an SCMFC could be used as a biosensor for BOD determination. A strong linear relationship between the total charge transferred and BOD concentration of sodium acetate in a range from 81 to 636 mg/L, with a coefficient of

determination (R^2) reaching 0.9977, was found. The correlation remains strong even when tested with real domestic wastewater having BOD concentrations of 178 and 253 mg/L. It is suggested that a unified linear correlation can be established for both artificial and real wastewater samples, with the coefficient of determination (R^2) exceeding 0.98. Despite the promising results, the coulombic efficiency remains less than expected, and this is a task for future research. Beyond factors related to the model's structure and operation, it is crucial to assess the impact of inhibitors on microbial activity and the performance of the SCMFC-based biosensor by analyzing the microbial community on the anode. Additionally, as the SCMFC has primarily been applied to municipal wastewater rich in easily biodegradable organics, further studies are needed to develop models applicable to various industrial wastewater types. These efforts aim to enhance the overall performance and versatility of the SCMFC-based biosensor for broader practical applications.

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CRedit authorship contribution statement. Dinh Thi Thu Ha: Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition, Supervision. Pham Ngoc Phat: Formal analysis.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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