



Short communication

Computational investigation of the flow field contribution to improve electricity generation in granular activated carbon-assisted microbial fuel cells



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H I G H L I G H T S

- CFD-multi order Butler Volmer reaction model is used to study porous anode.
- The addition of GAC improves the mixing by creating a uniform flow field.
- Such a flow field increases current by enhancing the convective substrate transfer.
- Improved flow field contributes to at least 17% of the current enhancement.
- New findings are instructive to MFC optimization on both design and operations.

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Microbial fuel cells (MFCs) offer an alternative approach to treat wastewater with less energy input and direct electricity generation. To optimize MFC anodic performance, adding granular activated carbon (GAC) has been proved to be an effective way, most likely due to the enlarged electrode surface for biomass attachment and improved mixing of the flow field. The impact of a flow field on the current enhancement within a porous anode medium (e.g., GAC) has not been well understood before, and thus is investigated in this study by using mathematical modeling of the multi-order Butler-Volmer equation with computational fluid dynamics (CFD) techniques. By comparing three different CFD cases (without GAC, with GAC as a nonreactive porous medium, and with GAC as a reactive porous medium), it is demonstrated that adding GAC contributes to a uniform flow field and a total current enhancement of 17%, a factor that cannot be neglected in MFC design. However, in an actual MFC operation, this percentage could be even higher because of the microbial competition and energy loss issues within a porous medium. The results of the present study are expected to help with formulating strategies to optimize MFC with a better flow pattern design.

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1. Introduction

Microbial fuel cells (MFCs) have been considered as a next-generation technology to recover electrical energy from wastewater, due to its advantages such as reduced energy consumption, minimal sludge production, and direct electricity generation [1]. In an MFC, organics are degraded by microbial consortia within an

anodic compartment, and the produced electrons are transferred to a cathodic compartment via an external circuit [2]. Because of the complex interaction between microbial, electrochemical and engineering factors, a good understanding of the anodic performance is key to MFC design and optimization [3]. The anode electrode plays an important role in electricity generation, and a large surface of the anode electrode is preferred for biofilm attachment. Several strategies have been employed to increase the electrode surface, such as modifying an anode electrode with nano-materials [4], using a pre-fabricated carbon brush [5], or adding granular activated carbon (GAC) [6]. Among those, GAC may be the most cost-effective approach because the material is inexpensive. GAC not

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only provides a large surface area for bacteria adhesion, but also increases the affinity for anodic substrates, resulting in better kinetic performance versus other electrode materials [7]. Packing GAC in an anode compartment also affects substrate distribution and liquid flow pattern, which has not been well understood before.

Computational fluid dynamics (CFD) can be used to simulate and predict fluid flow and species transport by solving the governing advection-diffusion equations. In the past decade, researchers have attempted to use CFD techniques to assess proton accumulation and substrate distribution by analyzing the hydrodynamics within the anodic compartment [8–11]. These studies proved that varying flow conditions is indeed a key factor to improve electricity generation due to the effects of convection on diluting accumulated protons and enhancing substrate distribution within the anodic compartment. However, none of these studies have attempted to examine the correlation between the varied hydrodynamic conditions and electrical generation within a porous anode.

To further understand improvement of electricity generation using GAC and quantify the contribution of flow field to the improvement, an established and validated multi-order Butler-Volmer equation [12] was applied to analyze the complex hydrodynamics and bioelectrochemical process in an anodic compartment packed with GAC. Comparing to other MFC models that usually integrate conventional Monod and Butler-Volmer equations [13], the multi-order Butler-Volmer equation is expected to provide a simple but realistic simulation. It is assumed that the addition of GAC can provide enough surface area for microbial adhesion and also change the flow pattern of the substrate and microbes within the bulk liquid. The present study aims to gain a deeper insight into the interactions among anode chamber configuration, fluid flow and MFC performance, and provide instructional advice on optimizing the design and operation of MFCs.

2. Materials and methods

2.1. MFC setup and operation

The MFC was constructed as a tubular reactor (32 cm tall and 3.8 cm inner diameter) made of anion exchange membrane (AEM-Ultrex AMI 7001, Membrane International, Inc, Glen Rock, New

Jersey, USA), resulting in a total anodic liquid volume of 350 mL (Fig. 1). Carbon cloth (Zoltek Corporation, St. Louis, MO, USA) was used as the material for both the anode and cathode electrodes. Before use, the carbon cloth was soaked in acetone solvent overnight and then heated for 30 min at 450 °C. The finished anode electrode (with effective surface dimensions of 22 cm-long and 2.9 cm-diameter) was installed along the inner surface of the AEM tube and supported by a plastic mesh. A total mass of 132 g of 4×10 GAC (Calgon Carbon Corp, Pittsburgh, PA, USA) was used as an additional electrode inside the AEM tube, resulting in a net liquid volume of 217 mL. The cathode electrode (23 cm \times 12 cm) was coated with Pt/C powder (Etek, Somerrest, NJ, USA) at a loading rate $0.3 \text{ mg Pt cm}^{-2}$, and wrapped the AEM tube. The anode and cathode electrodes were connected to a 10Ω resistor.

The MFC was operated at room temperature. Its anodic compartment was inoculated with anaerobic sludge from the Peppers Ferry Wastewater Treatment Plant (Radford, VA, USA) and fed with a synthetic solution containing (per L of tap water): sodium acetate 0.5 g; NH_4Cl 0.15 g; NaCl 0.5 g; MgSO_4 0.015 g; CaCl_2 0.02 g; KH_2PO_4 0.53 g; K_2HPO_4 1.07 g; and 1 mL trace elements [14]. No recirculation was applied to the anolyte, but the catholyte (50 mM phosphorus buffer solution) was recirculated at 5 mL min^{-1} . The flowrate of the anolyte was controlled by a peristaltic pump to achieve the desired hydraulic retention time (HRT) of 10 h.

2.2. Measurements and analysis

The MFC voltage was recorded every 5 min by a digital multimeter (2700, Keithley Instruments, Cleveland, OH). The pH was measured using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The concentration of chemical oxygen demand (COD) was measured by using a colorimeter according to the manufacturer's procedure (Hach DR/890, Hach Company, Loveland, CO, USA).

2.3. Computational model development

A steady, laminar, incompressible flow was assumed since the Reynolds number is 0.42 based on the inlet velocity of $1.44 \times 10^{-5} \text{ m s}^{-1}$. The conservation equations for mass and

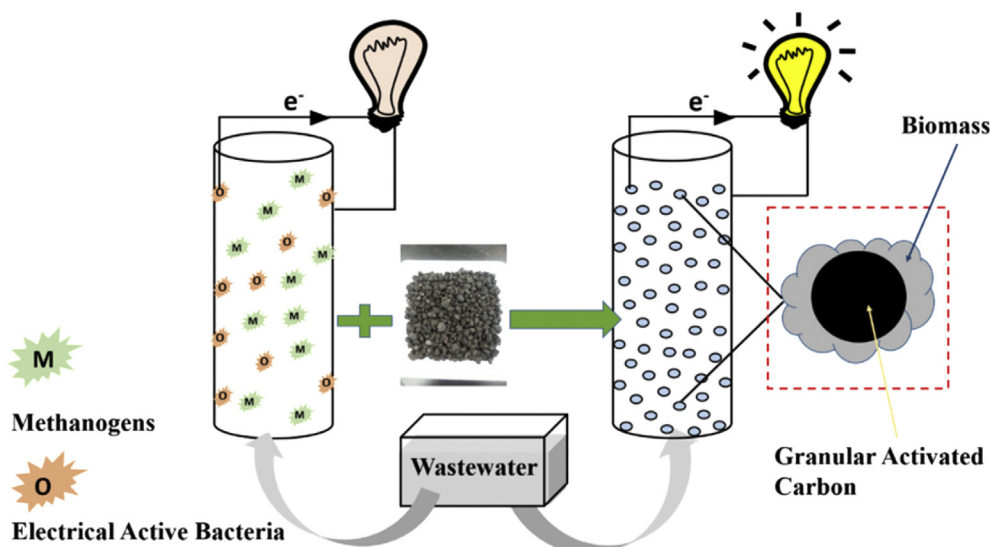


Fig. 1. A schematic of a tubular GAC-MFC operated with low-strength organic stream.

momentum, and species transport were solved using ANSYS Fluent (15.0). Based on the performance of the MFC described in Sec. 2.1, the computational model further assumed that only electroactive-bacteria produces electricity and the methanogens are non-electroactive, organic degraders. The electrical reactions were modeled using a multi-order Butler-Volmer-Monod equation, which has been validated and discussed in detail [12]. A direct contact between cytochrome on outer cell membrane and electrode surface was considered as a key process for electron transfer. The voltage generation was calculated as the gap between the open circuit potential (OCP) and potential loss (E_{int}). Because the cathodic performance is beyond the scope of the present study, a fixed potential (0.27 V vs standard hydrogen electrode) was assumed in the model. Therefore, potential losses come from the anodic compartment, which primarily includes mass transfer resistance, activation overpotential, and ohmic loss. More details about mass balance for substrate consumption, electron transfer mechanism, and electrical generation can be found in our recent study [12].

A porous media concept was also introduced to model the packed bed configuration of the GAC. It should be noted that formation of biofilm on electrode surfaces will introduce extra mechanical resistance to the flow field and build up the porosity. However, this factor is not included in this study due to lack of proper measurement methods for *in situ* monitoring of biofilm variation on complex media such as GAC. The porosity of the GAC measured in the experiments was 0.62, while the permeability k was calculated for a packed bed configuration:

$$k = \frac{D_p^2}{150} \frac{\varepsilon^3}{(1 - \varepsilon)^2} \quad (1)$$

where D_p is the average diameter of GAC particles equal to 1 mm and ε is the GAC porosity. It was assumed that GAC particles are covered exclusively by electro-active bacteria and biofilm. The growth of biofilm might create a diverse condition for the transport of electrons to the electrode surface; however, prior findings of bacterial nanowires indicate that biofilm could be highly conductive [15]. Thus, in this study, the biofilm attached on the electrode surface is assumed to be ideally conductive and all electrons generated from the anodic reaction are readily collected by the anode surface. By assuming a perfect spherical shape for all GAC particles, the surface-to-volume ratio is $b = 6/D_p$. For other electrode configurations where the electrode is not perfectly spherical or for nano-structured configurations [16], the surface-to-volume ratio b might need to be adjusted but the other parameters remain same.

The reaction rate r_g for the anode surface reaction occurring on the GAC surface can be transformed into a volumetric reaction in the bulk liquid:

$$r_g = r_{a,0} C_{ac}^\gamma \left[\exp\left(\frac{\alpha \eta_{act}}{RT}\right) - \exp\left(\frac{(\alpha - 1) \eta_{act}}{RT}\right) \right] b \quad (2)$$

where $r_{a,0}$ is the anode reaction rate constant and C represents the molar concentration for acetate (ac). The reaction order of the anode reaction γ has been determined to be 6.4. The other parameters include the transfer coefficient α , the activation overpotential on the reactive surface η_{act} , the universal gas constant R , and the room temperature T .

3. Results and discussion

3.1. MFC performance

The validity of the multi-order Butler-Volmer equation together with the CFD technique has been examined and verified in great detail [12]. In the present study, two operational conditions are tested: Case A using 0.5 g L^{-1} sodium acetate at a constant flow rate of 0.59 mL min^{-1} , and Case B operating with the same flow condition but filled with GAC particles inside the anodic compartment to form a packed bed GAC-MFC configuration. The numerical results are compared with the experimental data, as shown in Fig. 2. In general, the numerical results are in a good agreement with the experimental data. It is clearly demonstrated that the addition of GAC into the anodic compartment increases the current generation from 2.30 ± 0.33 to $6.29 \pm 0.60 \text{ mA}$ in the experiment, and the model predicts that the current increases from 2.48 to 8.21 mA (Fig. 2A). The slight deviation of the effluent COD might result from the overestimation of COD measurement because only the soluble portion of the total residual COD that included detached biomass was simulated by the model (Fig. 2B).

3.2. Quantification of contribution

Two factors could simultaneously contribute to the current enhancement with GAC addition, the increased biomass attachment and a uniform flow field, while the impact of the latter on the current enhancement remains unclear. To better investigate the effects of a uniform flow condition, an additional simulation is considered by assuming GAC as a nonreactive but porous medium,

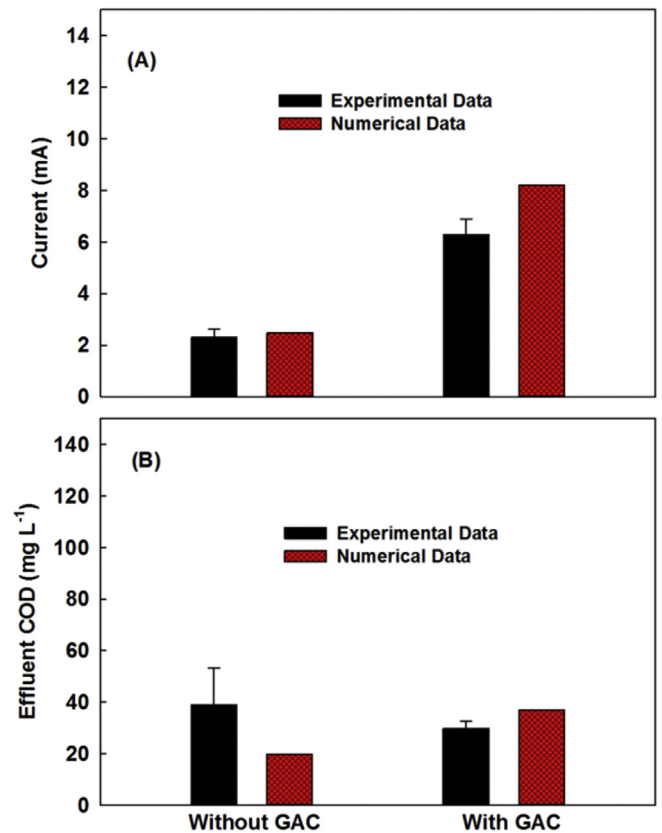


Fig. 2. Comparison of experimental and numerical data with an influent COD of 390 mg L^{-1} under absence (Case A) or presence (Case B) of GAC in the anodic compartment: (A) current generation; (B) effluent COD concentration.

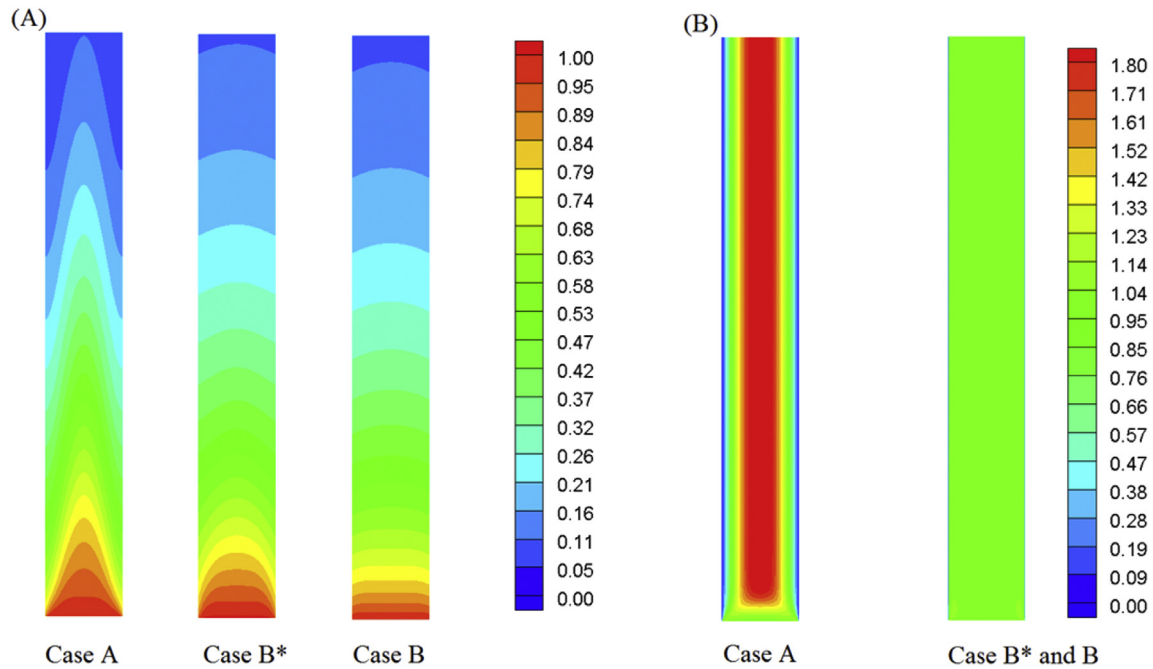


Fig. 3. Contours of (A) substrate concentration nondimensionalized by the inlet substrate concentration, and (B) vertical velocity nondimensionalized by inlet velocity.

denoted as Case B*. It should be noted that because the momentum equation is uncoupled from the species transport equation, both Case B and B* share the identical flow field but the substrate distribution is different. The results of three sets of substrate distribution contours and two sets of velocity contours are shown in Fig. 3. According to the multi-order Butler-Volmer equation (Eq. (2)) and electrical potential balance [12],

$$\eta = E_c - E_{a,0} + \frac{RT}{8F} \ln \left(\frac{C_{ac}}{C_b^2 C_p^9} \right) - V - IZ_{int} \quad (3)$$

the anode reaction rate, or the current production, is primarily determined by the local substrate concentration. However, a higher current would always lead to a smaller activation overpotential η_{act} , a key parameter to initiate the electrochemical reaction on the anode surface [17]. Therefore, to maximize the reaction rate and fully utilize the effective anode surface, a uniform substrate distribution is preferred. This can be accomplished by increasing the transport rate of substrate from the high concentration region to the low concentration region. In general, the transport of organics consists of two mechanisms, substrate diffusion and convective substrate transfer. The substrate diffusion rate is solely determined by the substrate concentration gradient and mass diffusivity; a simulation to predict substrate diffusion rate is beyond the scope of the current study. The Peclet number [18] can be used to characterize the relative strength of convective mass transfer to diffusive mass transfer.

$$Pe = \frac{Lu}{D} = \frac{\text{convective transport rate}}{\text{diffusive transport rate}} \quad (4)$$

where L is the characteristic length (reactor length of 0.22 m), u is the characteristic velocity (inlet velocity $1.44 \times 10^{-5} \text{ m s}^{-1}$), and D is mass diffusivity, which is usually on the order of 10^{-9} . In most engineering applications, the Peclet number is so large that the diffusive mass transfer can be neglected. In the current study, the Peclet number is on the order of 10^4 , thus the convective mass

transfer is dominant in the substrate transport. The convective transfer rate of substrate r_c , however, is basically dominated by the local velocity u and can be controlled, where:

$$r_c = \frac{\partial}{\partial x}(uC) \quad (5)$$

The present tubular MFC reactor has a regular pipe flow pattern, which shows a parabolic profile for substrate concentration along any cross-sectional area. Due to the boundary layer effects, the flow near the anodic surface shows almost a stationary state, which could impede the convective transfer of substrate to the reactive surface. Therefore, the substrate is distributed unevenly, and mostly concentrated along the centerline in Case A (Fig. 3A). However, after adding GAC to the anodic compartment, each GAC particle can exert shear stresses to the flow and intensify the momentum transfer. It can be seen in Fig. 3B that the flow field is more uniform in both Case B and B*, and the velocity magnitude of flow near the anodic surface has been enhanced dramatically. Consequently, an increased substrate transfer rate to the reactive surface is achieved. Comparing to Case A, which shows a steep substrate distribution along any cross-sectional area, Case B* benefits from the addition of GAC as a nonreactive porous medium and allows an increased substrate transportation rate from the centerline (high concentration region) to the reactive surface (low concentration region); then as a result, a relatively high current substrate concentration is achieved adjacent to the reactive surface, boosting the current production from 2.48 mA to 3.45 mA. In Case B, which is aided by reactive porous GAC, the horizontal substrate gradient becomes trivial due to the integrated effects of the increased substrate transport and enlarged biochemical reaction areas, and thus a high current of 8.21 mA is achieved. Therefore, it can be concluded that by adding GAC into the anodic compartment, two-fold functions can be achieved, including (1) a more spacious reactive surface for biomass attachment, and (2) an optimized substrate distribution within a uniform flow field. The difference between Case A and Case B* suggests that the uniform flow field has contributed at least 17% of the total current production increment

(the difference between Case A and Case B). It should be noted that this is still a conservative estimation regarding the contribution of the flow field because of the assumptions that the GAC particles are ideally conductive and exclusively and entirely attached by biofilm in the simulation.

The finding of this study has demonstrated, for the first time, the quantitative contribution of a flow field generated by using GAC to the enhancement of electricity generation in MFCs. In a regular MFC that does not have porous electrode media, better mixing can be guaranteed by increasing the electrolyte recirculation, resulting in a higher energy demand by the pumping system; this may be avoided by the addition of GAC that can offer an effective way to boost the current gain in MFCs. This finding has several implications to MFC development. First, the contribution of a flow field to enhance electricity generation is not minor and thus should be taken into consideration when designing an MFC. In the past, the emphasis was put on increasing the surface area of an electrode, which would not necessarily alter or optimize the flow pattern. For example, modifying an electrode with nanomaterials has very minor effects on changing the flow pattern. Future designs should consider both surface area and uniform flow. This may be accomplished by adding media to an anode compartment that only has plain electrodes (e.g., carbon paper/cloth modified with nanomaterials), or modifying the electrode that already creates a better flow pattern (e.g., GAC or carbon brush) with high surface area materials (e.g., nanomaterials). Second, understanding the effect of a flow field on electricity generation may reduce or eliminate conventional recirculation. Previous studies have demonstrated that internal recirculation could be an effective approach to enhance electrical generation, but it also significantly increased the energy consumption [19]. Having an optimal flow by using porous media or a pre-designed flow pattern could offer an effective approach to improve substrate distribution and thus reduce the need for recirculation, resulting in less energy consumption. This is especially important to MFC scale-up and long-term operation with actual wastewater, considering that energy output could be low (thus, to achieve energy neutral or plus, energy consumption must be greatly reduced). A recent study demonstrated that a 200-L MFC system using a carbon brush as the anode electrodes but without the anolyte recirculation could offset some of the energy consumption by using the produced electricity to treat the primary effluent [20]. The contribution of a uniform flow with electrode materials other than GAC will certainly be of great interest to future studies. Third, the accumulation of biomass on GAC surfaces and membranes may affect the MFC performance, although such an effect may not be very serious (with carbon brush electrodes) according to our prior studies of long-term MFC operations with actual wastewater [20,21]; biofilm formation on complex media like GAC warrants further investigation. Last but not least, although the influence of the flow field on the fate of other compounds such as ammonium ions was not analyzed in the present study, we expect that large changes in the flow field could generate an impact on ion transport from an anodic compartment to a cathodic

compartment, which may be relevant to current generation by affecting electrolyte resistance [22,23].

4. Conclusions

In the present study, the multi-order Butler-Volmer equation has been employed with CFD to understand the interrelationship between the flow field and electricity generation in a GAC-MFC. It is found that altering the flow pattern with GAC addition could increase the current production by at least 17%. This result has important implications to future design of the anode electrode for MFCs by considering both increasing surface area and optimizing flow pattern, and to MFC operation by reducing liquid recirculation and thus decreasing the associated energy consumption.

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