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Original Research

Influence of Initial pH on Anodic Biofilm Formation in Single-Chambered Microbial Electrolysis Cells

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Abstract

This study investigates the influence of initial pH on anodic biofilm formation of microbial electrolysis cells. Initial pH affects the activities of microorganisms in MEC, and furthermore will affect hydrogen (H_2) generation. Therefore, we explore the effects of initial pH on anodic biofilm formation of microbial electrolysis cells and the intrinsic reasons. In a single-chamber MEC, with different initial pH (which are 5.0, 6.0, 7.0, 8.0, and 9.0), the maximum power density during the enrichment process was 2.73 mA/cm^2 at pH 8.0, which is 56% and 23% higher than those working at pH 7.0 and 9.0, and get worse under acidic conditions. pH 8.0 also showed the highest coulombic efficiency of 46.4% compared with other experimental groups, and energy recovery efficiency is 17.5%. Membrane biomass, as an indicator for anode microbial biomass, decreased sharply at pH 5.0 and 6.0 compared with the neutral and alkaline. Scanning electron microscopy verifies that alkalescent conditions are beneficial to form more rod-shaped bacteria in MECs. These results show that electrochemical interactions between bacteria and electrodes in MECs are enhanced under neutral and alkaline conditions, and the optimal initial pH for anode bacteria formation of 8.0. The information provided below will be useful for improving MEC hydrogen generation.

Keywords: initial pH, microbial electrolysis cell, anodic biofilm, electroactive microorganism, hydrogen production

Introduction

The microbial electrolytic cell (MEC) is a device that uses an anodic electroactive microorganism to degrade organics in order to produce electrons and convert protons into hydrogen or other substances in the cathode, in this device the hydrogen can be sustainably produced from biodegradable compounds contained in wastewater. Thereby MEC will achieve wastewater treatment simultaneously [1]. Although being an emerging technology, the biggest drawback of practical meaning of the application of MEC is that the hydrogen production is inefficient [2, 3]. To achieve a higher conversion of a substrate to hydrogen, much effort has been exerted on increasing hydrogen production by

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the application of MECs with optimizing operation parameters, such as applied voltage, reactor type, electrode type, reaction conditions [4-10], etc.

Besides the aforementioned parameters, the bacteria in the MEC reactor will only grow under a specific range of pH and salinity, so the pH of a solution should be in a certain range. As the anode-respiring bacteria produce protons and electrons, which will acidify the anode solution, the lower pH environment will have a significant inhibitory effect on the anode electrochemical microbial community [11]. Liu et al. found that hydrogen yield decreased after the impact of low pH shock on MEC anodic biofilm [12]. When protons reach the cathode and accept electrons, they will transfer from the anode through the outer circuit and produce hydrogen gas, which will cause the cathode to be alkaline. Zhuang et al. discovered that the alkaline anodic pH conditions resulted in a more negative anodic potential, which in turn caused higher current density of microbial fuel cells (MFCs) [13]. In general, the MEC system has a significantly pH change during the reaction process. At present, a certain concentration of phosphate buffer (50~100 mmol·l^{-1}) will be applied to the MEC system to provide better ion strength and maintain a neutral environment [14, 15]. Based on the Nernst equation and characteristics of a typical solution, a pH gradient of cathode and anode in a two-chambered MEC reactor will result in a voltage loss of about 60 mV [16]. Therefore, pH is an important factor influencing the effect of MEC.

In this study, we aim at finding the effect of different initial pH on anodic biofilm formation of MEC. And electrochemical techniques analysis will be applied to study the electron transfer kinetics of anodic biofilms in MECs. For example, Katuri et al. investigated the surface electron transfer of Geobacter sulfurreducens anodic biofilms during different periods by cyclic voltammogram (CV) [17]. Furthermore, the mechanism through exchange current density and electrode potential is explained, to be specific, the amount of anode electroactive microorganism was determined by detecting the phosphorus content in the anode biofilm, and scanning electron microscopy is used to explore the morphology of biofilms formed under various initial pH conditions. This study is one of the few efforts to explore an optimum initial environmental pH value for enriching the anodic bacteria biofilm formation, which may provide a theoretical basis for future research and application of MEC in practical projects.

Material and Methods

MEC Configuration

The MEC was made of glass with a cylindrical shape, and with a diameter of 90 mm and a height of 100 mm (empty bed volume of 500 mL), in which the electrode chamber had a water inlet and an outlet, while at the top of it there was a gas outlet and a socket of electrode. The anode was made of a graphite flake (30*30*2mm) that was intertwined through holes drilled into a stainless steel frame that was used as the anode module placed in the center of the chamber. The graphite flakes were pretreated with nitric acid (1N), acetone (1N), and ethanol (1N) for 1 day each, and then were washed with MilliQ water. The cathode electrode was made of a titanium alloy sheet with a surface area of 9 cm^2 and a Pt catalyst (0.5 mg/cm^2), and it was placed on the opposite side of the chamber. They were held together by plastic screws and spaced for 3 cm between each other. Furthermore, they were connected to an external circuit with titanium wires. The positive pole was connected to the anode by connecting with a programmable power supply and the negative pole was connected to the cathode by connecting with the same supply. An online recorder instrument was applied to this study to record the electric current. The configuration of the reactor is shown in Fig. 1.

MEC Inoculation and Operation

The sludge in the MEC was taken from the secondary sediment of pig manure as raw material of anaerobic fermentation (College of Energy and Environmental Sciences, Yunnan Normal University, Kunming, China), and the weight of inoculated sludge for each chamber was 100 g. The inflow of the MEC chamber was compounded with 6 g sodium acetate. The medium consisted of 100 mL of synthetic wastewater (SWW) composed of KH_2PO_4 6.1 g/L; $K_2HPO_4{\cdot}3H_2O$ 9.6 g/L; KCl 2.22 g/L; NH_4Cl 0.28 g/L; yeast extract 0.1 g/L; $MgSO_4{\cdot}7H_2O$ 0.1 g/L; $CaCl_2{\cdot}2H_2O$ 10 mg/L; and 5 mL of a trace element mixture with the following composition: $(NH_4)Fe(SO_4)_2{\cdot}6H_2O$ 3.96 g/L; H_3BO_3 0.05 g/L; $ZnCl_2$ 0.05 g/L; $CuCl_2{\cdot}2H_2O$ 0.04 g/L; $MnCl_2{\cdot}4H_2O$ 0.05 g/L; $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ 0.05 g/L; $AlCl_3{\cdot}6H_2O$ 0.09 g/L; $CoCl_2{\cdot}6H_2O$ 0.05 g/L; $NiCl_2{\cdot}6H_2O$

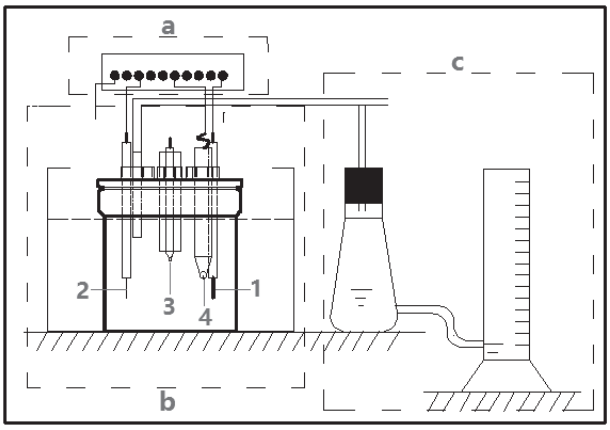

Fig. 1. Single-chamber MEC shown with online recorder: a) fermentation chamber, b) gas collection unit, c) anode electrode, 1) cathode electrode, 2) pH electrode, and 3) Ag/AgCl reference electrode.

0.09 g/L; and a multivitamin. The total mixed liquor in the reactor was 400 g.

MEC anode bacteria enrichment was operated in five consecutive batch modes and the initial pH was set at 5.0, 6.0, 7.0, 8.0, and 9.0, respectively. Then the reactor was put into a water bath kettle in a condition of constant temperature at 35ºC and an applied voltage of 1.0 V. To ensure the condition was anaerobic, ultra-pure nitrogen was sparged into the chamber for 10 min at the beginning of each batch cycle to replace the air. We controlled for different initial pH respectively when the reactor condition was stable and the electric current reached its maximum, the liquids in the anode and cathode chamber were going to be emptied and refilled with the medium, which corresponded to the anode bacteria enrichment process (no inoculation), and other external conditions were consistent, the hydrogen production under the anode biofilms enrichment was going to be tested. Magnetic stirring was involved in this experiment.

Analyzing Projects

The applied voltage was collected with a voltage-stabilized power supply (TXN-1502D, Shenzhen, China). The electric current was recorded by online recorder (R7100-A08, Shanghai, China). The biogas composition, including hydrogen, methane, and carbon dioxide was measured by a gas chromatograph (GC9790II, Zhejiang, China) with a thermal conductivity detector (TCD). The volatile fatty acids (VFAs) contents were measured by a gas chromatograph (GC9790II, Zhejiang, China) with a flame ionization detector (FID).

MEC anode bacteria enrichment changed the electrode potential and the target pollutant oxidation reduction peak. To determine the electroactivity of the anode biofilm in SWW, a cyclic voltammetry (CV) scan in a three-electrode system was applied, and the anode enriched with bacteria was the working electrode. Ag/AgCl was taken as the reference electrode and the cathode as the counter electrode, the reference electrode was placed in the test chamber. Electrode potential was measured by a multimeter with an Ag/AgCl electrode, and all potentials will be referred to the standard hydrogen electrode (SHE) (reference electrode) in this paper. Before starting each impedance measurement, the MEC was operated in discharge condition for over 30 min in order to reach a steady-state condition.

The phosphorus content in the anode biomass membrane was determined by phosphorus molybdenum blue spectrophotometry after pretreatment and digestion, and absorbance was measured at 700 nm wavelength.

After the test, anode samples were soaked by 2.5% glutaraldehyde solution for 30 min, then dried and coated with gold [18]. Samples were observed in a scanning electron microscope (JSM-6390, Japan) to describe the morphology of biofilms.

Hydrogen Production Calculations

The volume of hydrogen (V_{H2}) contained in the biogas was calculated using the following Eq. (1) according to the following relation suggested elsewhere [19]:

$$V_{\mathrm{H2}} = (H_s + V_{T,t})G_f \tag{1}$$

…where $V_{T,t}$ is the total volume of biogas produced, composed of H_2, CH_4, and CO_2; G_f is the hydrogen gas fraction contained in the biogas measured by the gas chromatograph; and *H*s is the spare volume of the reactor (ml).

The performance of each electrode was analyzed by calculating the cathodic and the coulombic hydrogen recoveries R_{CE} using Eq. (2). Coulomb efficiency can be defined as the ratio of the electron amount required for the reduction product of the electron quantity produced by the consuming donor. For the cathode, this indicates the amount of electrons converted into hydrogen in the cathode.

$$\mathrm{R_{CE}} = \frac{\eta_{CE}}{\eta_{\mathrm{th}}} \tag{2}$$

$$\eta_{CE} = \frac{\int_{t=0}^{t} I\mathrm{d}t}{2F}$$

$$\eta_{\mathrm{th}} = 8\mathrm{n} \tag{3}$$

…where η_{CE} is the ratio of the moles of hydrogen that can be recovered based on the current (*I*) measured under electrolysis time (d*t*), *F* is the Faraday constant (*F* = 96,485 C/mole$^-$), and η_{th} is the maximum moles of hydrogen produced with the substrate consumed.

Energy recovery efficiency (η_E) based on the energy input and output ratios was calculated using the following equation:

$$\eta_E = \frac{V_{H2} \times Q_{H2}}{W_{\mathrm{in}}} \tag{4}$$

$$W_{\mathrm{in}} = E_{\mathrm{ap}} I\mathrm{t} \tag{5}$$

…where W_{in} (J) is the electrical energy input, Q_{H2} (12.86J/ml) is the hydrogen gas calorific value, E_{ap} (V) is the applied voltage to the system by the power supply, and *I*(A) is the current during the batch cycle.

Results and Dscussion

Electroactivity Performance during the Formation of Anodic Biofilm

The profile of the batch current density of different initial pH is illustrated with Fig. 2. The current was

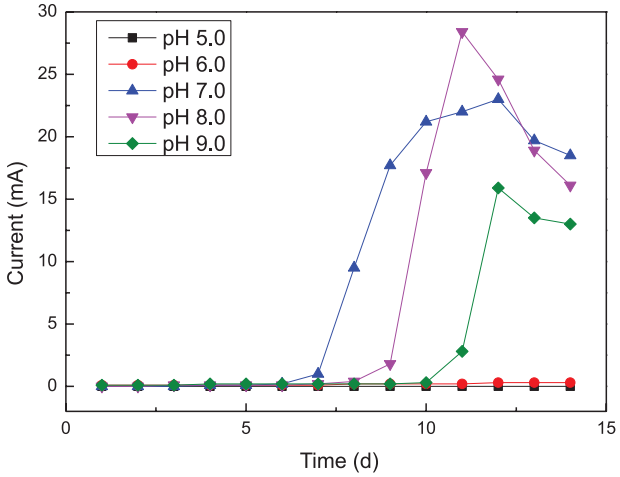

Fig. 2. Current production under different initial pH.

varied when the initial pH changed. During the start-up period, the current stayed at zero for 3~5 d, and then the experimental group under the initial pH of 6.0, 7.0, 8.0, and 9.0 started to increase until it was 0.1, 1.1, 0.3, 0.1 mA, respectively, and the current would increase directly (without lagphase) over time. Maximum current peak of 28.4 mA was obtained at pH 8.0 with a current density (the area of the flake graphite was 9 cm^2) of 3.16 mA/cm^2. In contrast, a maximum current peak of 23.0 mA was obtained at pH 7.0, with a current density of 2.56 mA/cm^2, and 18.9 mA was obtained at pH 9.0 with a current density of 2.1 mA/cm^2. The comparatively slower rate for the current to peak in the pH 9.0-operated MEC denoted that the electroactive microorganism cannot reproduce effectively in an alkaline environment. However, the pH of 6.0 was only 0.3 mA and pH of 5.0 experimental group did not generate any current. It was obvious the stable current would go up under weak alkaline and neutral environments. In addition, current rise indicated that the anodic electroactive microorganisms were effectively attached to the anode.

Bard and Faulkner indicated that the adhesion of the biofilm would change the electrode potential of the anode, and electrode potential may reflect the electrode activity of the positive and negative equilibrium state [20]. The individual electrode potentials were also measured and shown in Fig. 3. Because the cathode used the same material, the design results in the cathodic potentials were almost identical in all cases. However, the enrichment degree of biofilm made the anodic potentials varied. The anode at initial pH 8.0 and 7.0 had the maximum anode electrode potential among the entire current range, while the anode at initial pH 6.0 had the lowest anode electrode potential. This indicates that under the operational conditions of MEC, the bacteria with electrochemical activity can attach to the anode surface, which reduces the activation internal resistance of the electrode. In addition, Fig. 3 shows that the electric potential of the anode is greatly affected by the current. In other words, the anode potential increases with the increase of current.

Fig. 4 shows the cyclic voltammogram (CV) obtained for the flake graphite electrode after bacteria enrichment with acetate as the substrate at various pH, in the same potential amplitude (-0.8 to 0.8) and with a scan rate of 0.01V/s, the oxidation reduction current changes over time. CVs are extensively used to evaluate the bioelectrocatalytic activity of anode biofilms toward substrate oxidation, which indicated catalytic oxidation of the substrate by five biofilms and the heterogeneous electron transfered from the bacteria to the electrodes [21]. In the voltammogram with no cycle of biofilm forming on the electrode, there were no oxidation and reduction peaks. However, there was an obvious anode peak potential of the oxidation process at the initial pH of 7.0, 8.0, and 9.0, and the peak potential of the oxidation

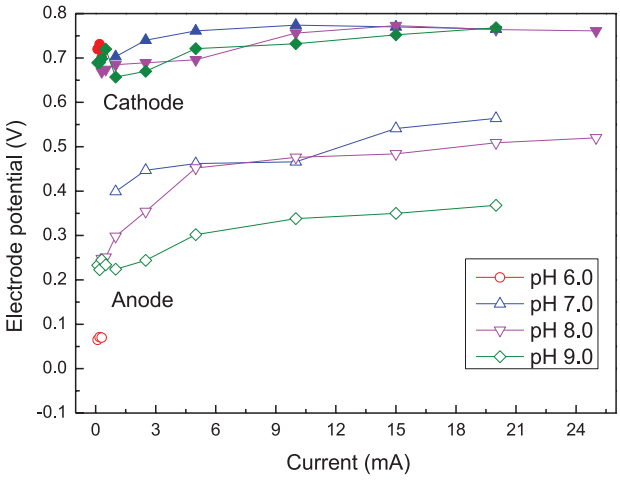

Fig. 3. Anode potentials (vs. Ag/AgCl) as a function of different initial pH.

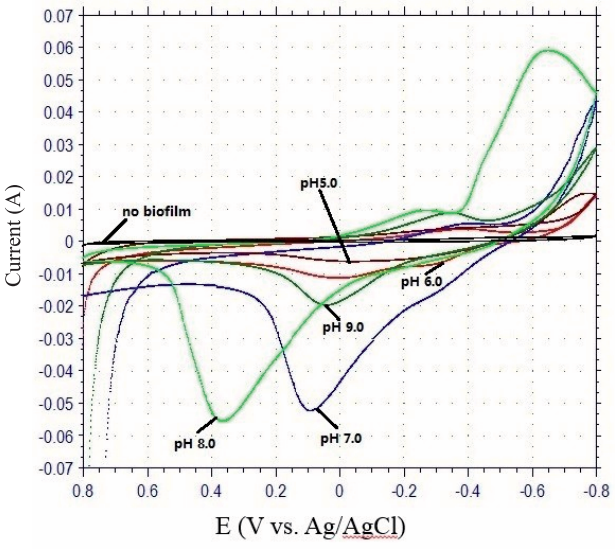

Fig. 4. CV responses of anodic biofilms to acetate oxidation under various pH conditions at a scan rate of 0.01V/s.

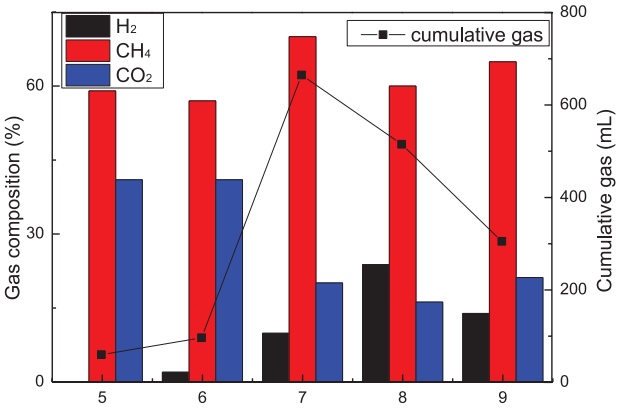

Fig. 5. Gas composition and cumulative gas volume of different pH.

process appeared at 0.1~0.4 V. Busalmen, Nunez, and Feliu indicated that this oxidation peak potential may belong to the outer membrane c-type cytochromes of OmcB, which participated in electrons transferring from electroactive bacteria to solid electrodes (anodes) and made it more convenient [18, 22]. According to Ohm's Law (R = V/I), under equal voltage, the greater the redox current between the carbon anode and the platinum electrode, the smaller the internal resistance between these two electrodes. The catalytic currents shown in Fig. 4 varied in the five cases. The highest catalytic current was 65.73 mA, observed from the biofilm enriched at pH 8.0. In comparison, the highest catalytic current was 49.49 mA at pH 9.0, 36.81 mA at pH 7.0, and 17.40 mA at pH 6.0, whereas the lowest one was 10.59 mA observed from the biofilm enriched at pH 5.0. The results of cyclic voltammogram in this study are in good agreement with those reported by Yuan et al. Redox processes of these redox active species are pH-dependent, in which neutral and weak alkaline environments are also determined to be favorable for

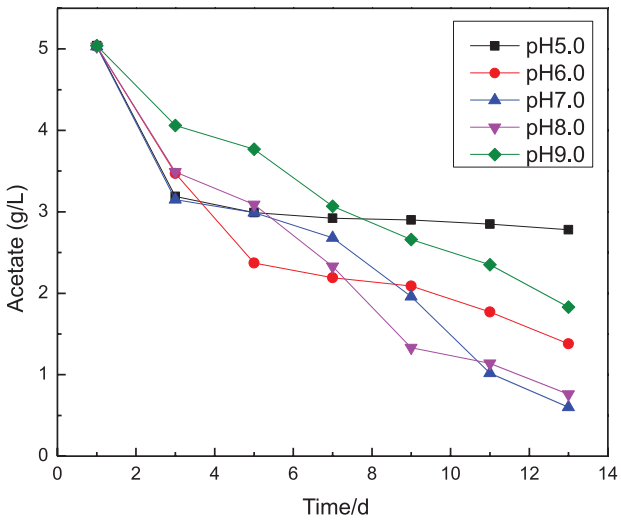

Fig. 6. Acetic content in different initial pH changes with time.

the most electrochemically active biofilm enrichment in single-chamber MECs.

Hydrogen Production of the Formed MEC Anode Membrane and Energy Efficiency

The anodes enriched with biofilm were used to produce hydrogen in microbial electrolysis cells, and they operated at different initial pH with the aim of finding better initial pH conditions for the anode biofilm formation. The hydrogen yield changed with different initial pH as it was shown in Fig. 5. The hydrogen yield began to increase from pH 6.0 and reached the top of 122.5 mL at pH 8.0, then decreased to 42.5 mL at pH 9.0. However, there was no hydrogen production at the initial pH of 5.0. The trend of hydrogen yield variation was similar to the change of current production, both of them reaching a maximum at the neutral and alkaline environments.

Fig. 6 shows the acetate removal efficiencies in different initial pH. The acetate removal efficiency first increased, then decreased with the initial pH from 5.0 to 9.0. Acetic consumption was the slowest at pH 5.0 and the removable efficiency was only 44.7%. Furthermore, it reached the top with 88.1% under the initial pH 7.0; however, hydrogen production did not reach the top at pH 7.0, which was due to a large amount of methane-producing bacteria being active in a neutral environment. After that, it decreased to 84.9% at pH 8.0 and 63.6 at pH 8.0, but the corresponding hydrogen production got the first and the second ranks. Based on these results, the biofilm, which was formed at neutral and weak alkaline environments, had positive effects on acetate removal, which also proved that the biofilm formed at pH 8.0 exhibited more hydrogen-producing electrochemical microorganisms compared with other anodic biofilms.

Cathodic hydrogen recovery depends on both conditions in which the hydrogen recovered and the electrons transferred from the anode to the cathode, which is influenced by the anodic electroactive microorganism activity, and hence they varied with the change of initial pH. According to the cathodic reaction, the more the electrons are transferred to hydrogen, the higher the coulombic efficiencies (R_{CE}) and energy recovery efficiencies (η_E) will be [23]. In this study, the R_{CE} and η_E first increased before decreasing, which was similar to the acetate removal change with the different initial pH as shown in Fig. 7. Because there was no current in the experimental circuit in which there is no hydrogen production, the R_{CE} and η_E of initial pH 5.0 was not discussed. The R_{CE} for pH 6.0, 7.0, 8.0, and 9.0 were 12.5%, 37.4%, 46.4%, and 29.7%, respectively. Differences in the coulombic efficiencies revealed that the efficiency of anodic biofilm's electrons transferred to cathode to produce hydrogen in acid environment was not as efficient as a neutral and weak alkaline environment. Energy recovery efficiency increased to 6.0%, 11.2%, and 17.5% at pH 6.0, 7.0, and 8.0,

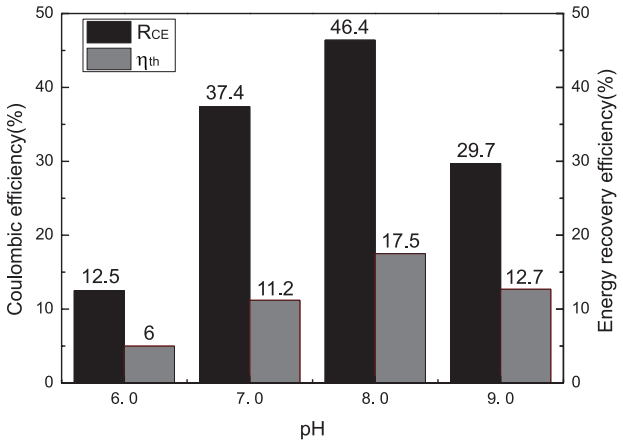

Fig. 7. Coulombic efficiencies (R_{CE}) and energy recovery efficiencies (η_E) in MEC cultivated with different initial pH.

respectively, while decreasing to 12.7% at pH 9.0. Energy recoveries were significantly correlated with initial pH over this range, which sharply decreased in acid environment. The highest η_E was 17.5% and it was obtained from the biofilm enriched at pH 8.0. Both coulombic efficiencies and energy recovery efficiencies were low in the neutral and alkalescent experimental groups, which resulted from an increase in methanogenesis at the increased reaction times. The results agree with the findings in the MEC tests, supporting the fact that the most electrochemically active biofilm is achieved under neutral and weak alkaline conditions.

Determining Anode Biofilm Biomass

In the process of hydrogenation of MEC, the electroactive microorganisms in the anodic biofilm produce the protons, electronic, and CO_2 by degrading the substrate. The electron passes through the extracellular electron to produce hydrogen by combining the cathode with the proton. Therefore, the quantity of anode microbial biomass is directly related to the production of electricity and hydrogen production. The number of microorganisms in the anode biofilm was determined by phosphorus molybdenum blue spectrophotometry, and the content of electroactive microorganisms was calculated through PO_4^{3-}-P concentration according to the standard curve of phosphate concentration. By pre-treating and dissolving anode biofilm, the author tested its absorbance by spectrometer at a wavelength of 700 nm. Table 1 shows that the phosphorus content was measured on each anode surface, which shows that the anode is enriched with microorganisms. The number of anode microorganisms in different pH conditions varies, with the anode at initial pH 7.0 having the maximum biofilm content, followed by pH 8.0. By comparison, the content of biofilm was poor in an acidic environment. This shows that weak alkaline and neutral conditions are more suitable for electroactive microorganisms in anodic enrichment. The biofilm formed at initial pH 7.0 contains the largest microbial biomass but did not exhibit the best electrical activity, which may be due to the anode biofilm also containing methane-producing bacteria. There are also studies indicating that electrobiogenesis can establish an electric syntrophy relationship with methane-producing bacteria and co-consume acetic to produce methane. This is also the reason for the detection of methane in all the tests [24, 25].

Scanning Electron Microscopy Images of Anode Biofilms

To evaluate the effects of initial pH on bacterial formation on the anodes, the morphology of biofilms was explored by scanning electron microscopy (SEM), as shown in Fig. 8. The anode before (Fig. 8a) and after (Fig. 8b-f) enriched with bacteria was also observed by this technique, and this confirmed that the microorganism morphology and quantity of the anode surface attached under different initial pH environment. The change of electrode potential and current density in the cyclic voltammetry was due to the degree of adhesion of microorganisms. And there was a large number of rod-shaped bacteria attached on the surface of the anode at pH 8.0. In comparison, there was a decrease in the number of bacteria attached on the anode at pH 9.0. The initial pH of 7.0 corresponding to the anode surface bacteria had a rod-shaped or elliptical shape, and the surface was attached to a layer of material, which may be the sludge in the formation process. However, there were almost no rod- or elliptically shaped bacteria on the electrode at pH 6.0 and 5.0. This result indicates that neutral and alkalescent provide a better environment for bacterial growth in MEC, especially at pH 8.0.

Table 1. The number of microorganisms in the anode biofilm under different pH.

pH	5.0	6.0	7.0	8.0	9.0
Absorbance(A)	0.756	0.797	2.009	1.179	0.850
Phosphate(μg/mL)	1.27	1.34	3.41	1.99	1.43
Microbial population/mL	3.93×10^{12}	4.15×10^{12}	1.06×10^{13}	6.18×10^{12}	4.43×10^{12}

Note: The organic phosphorus in the anode biofilm was converted to inorganic phosphorus through digestion and extraction; 1 nmol of phosphorus are equivalent to about 10^8 microbes in the size of escherichia coli

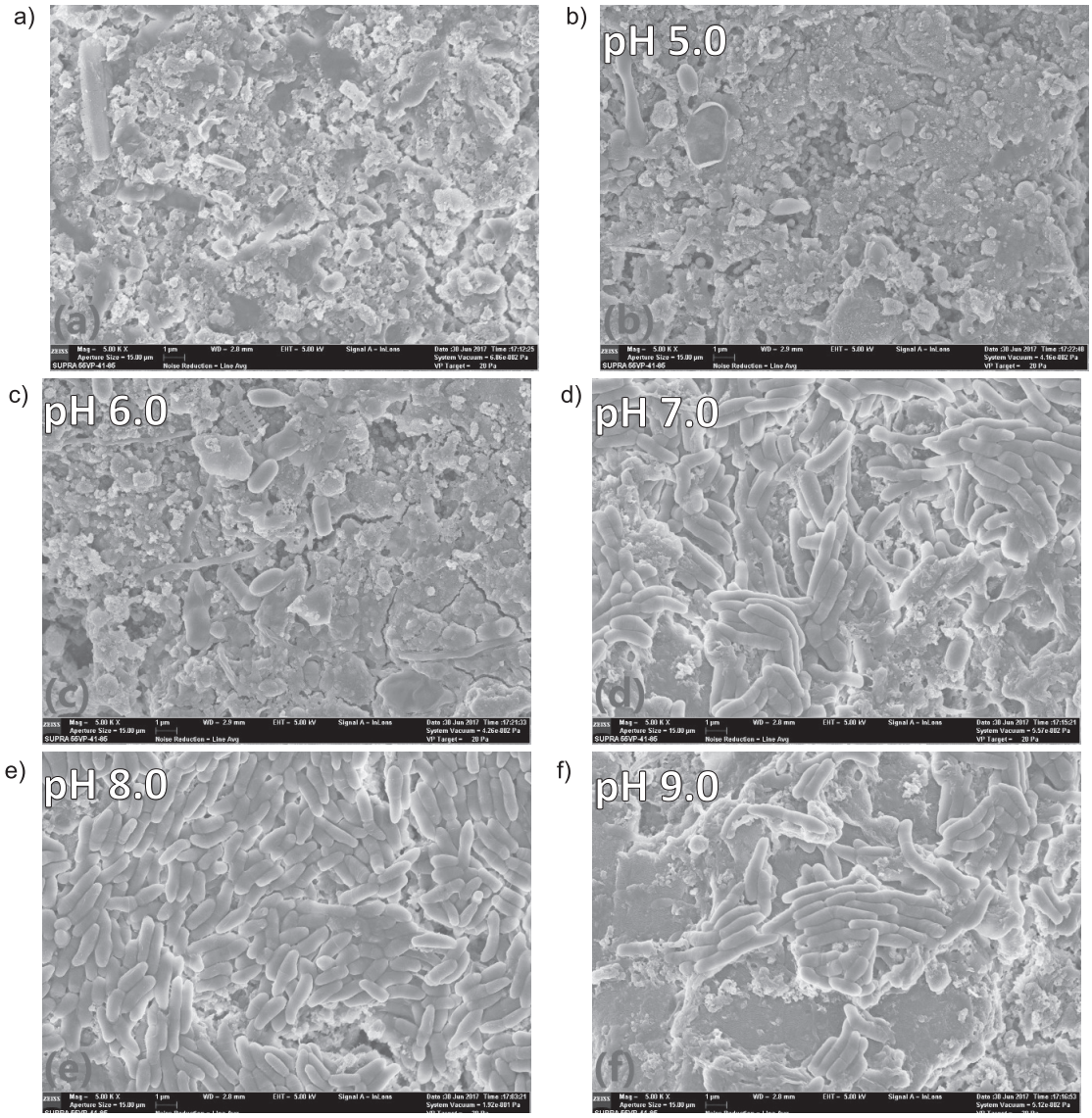

Fig. 8. Scanning electron microscopy image of the graphite flake electrode with various initial pH before enrichment a) and after bacteria enrichment (b-f).

Conclusions

This study mainly focused on comparing different parameters in MEC anodic biofilm enrichment under different initial pH (which were 5.0, 6.0, 7.0, 8.0, and 9.0). The biofilm formation in both neutral and alkalescent conditions showed that electron transfer efficiency was related to the electrocatalytic current, extracellular electron transfer rate, hydrogen production, energy efficiency, and anode biofilm biomass. Furthermore, the biofilm at pH 8.0 exhibited the best overall performance, whereas the acidic-culture MEC showed the worst performance. Meanwhile, SEM revealed the thriving growth of bacteria derived from anaerobically activated sludge under alkalescent conditions. The findings indicated that pH 8.0 may provide the optimum initial pH to enrich an MEC anodic biofilm.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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