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Simulation Biomass Effecting On Microbial Fuel Cell Electricity Properties and Substrate Degradation

Xingguan Ma[1], Jiao Wang[2], Xiangxin Xue[3], Yulan Tang[4], Jinxiang Fu[5]
[1,3]School of materials and metallurgy, Dongbei University, Liaoning Shenyang 110168, China
[1,2,4,5]School of Municipal and Environmental Engineering, Shenyang Jianzhu University,
Liaoning Shenyang 110168, China
Corresponding author, e-mail: [1]hj_mxg@sjzu.edu.cn, [2]woaijinglin521@sohu.com, [3]symxg@163.com,
[4]tyl98037@163.com, [5]hj_jxf@sjzu.edu.cn

Abstract

Microbial fuel cell (MFC) mathematical model was established with suspended microorganisms, biomass on the electrode material, soluble chemical substrates and intermediary. By simulating the process of the substrate degradation, biomass growth and the electric current production process, With different initial biomass concentration, suspended microbial biomass and biomass attaching on electrode varying with time, current and charge varying with time, substrate concentration varying with time and mediator concentration varying with time were investigated. The results showed that initial suspended microbial is little, growth of biomass is main on electrode, biomass in solution grow slowly, producing electricity the main function biomass is on electrode, while initial suspended microbial concentration is high, growth of biomass is main in solution, biomass on electrode grow slowly, producing electricity the main function biomass is in solution; the more initial suspended microbial, the faster current reaching the maximum, the more charge, the faster substrate degradation, the faster mediator variation; initial add biomass benefit to MFC producing electricity.

Keywords: *microbial fuel cells, simulationn, current, charge, biomass, substrate, mediator*

1. Introduction

Energy shortage and environmental pollution have become two significant global crises, and it has serious threaten to human living surrounding and development [1]. Microbial fuel cell (Hereinafter referred to as MFC) which function is to produce synchronous electricity and to degrade organic pollutants. There is great significance on solving the environmental pollution and the energy shortage. MFC as a new clean energy technologies production, play a key role on not only the treatment organic wastewater, but also producing electricity. The advantages by following: operating under mild conditions, controlling simple and producing nonpolluting product, and etc [2], so recently, it gets more and more attention. The research for MFC still remains at the experimental stage, but Only through the MFC experiment is difficult to fundamentally reveal the laws of MFC synchronization electricity and biological growth and organic pollutants degradation. Therefore at present some scholars are dedicated to study the mechanism of MFC through the method of the mathematical simulation [3] by anglicizing the process of electrochemical and biochemical, proposed a electrochemical pattern based on experiments [4] et al, create the MFC mathematical model by computer simulation, simulate current, voltage, bottom material matrix, the growth of micro-organisms evolved over time under different operating conditions and investigate the initial substrate concentration, medium concentration, oxidation-reduction potential, external resistance and other aspects of the battery, the simulation results are in good agreement with experimental results [5], et al, reveals that one of the most efficient ways is MFC computer simulation by rational designing and using.

But so far, there is not still systemic and in-depth way to study all the MFC factors which affect the biomass concentration on the production electricity and the substrate degradation. Biomass is the power to consume the substrate matrix in MFC, is also an important factor affecting on the production electricity and one of the important substance handling contaminated sewage. Therefore, this article establishing MFC anode chamber model, through the simulation of organic degradation process on MFC anode room, study initial biomass concentration on affecting the laws of microbial growth in anode solution and on the anode, the laws of

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degradation of organic pollution, the laws of MFC producing electricity and the laws of intermediary changing [6-8].

2. Research method
2.1. Reaction mechanism
In MFC reaction process exist generally electrochemical and biological chemical reactions phenomenon. The MFC electrochemical reaction is said a electron transfer relationship between the microorganism, electron donor and electronic receptors. As electron donor organic matter, under the microorganism function release electronic, the electronic through the direct or indirect way removed to the anode surface as electron acceptor. In electrochemical reaction process with a series of biochemical reactions, the biochemical reaction in the cells make bacteria metabolism, biomass accumulation, and reduce substrate. Microbial oxided substrate producing energy stored in the cell mitochondria by NADH and NADPH. NADH and NADPH is electronic carry body from substrates to metabolism product, in anaerobic conditions, it has high efficiency electrical activity, which can be directly or indirectly discharge cells [9] [10]. And the response of the electrode surface decide on MFC performance, making sure to electrode surface material concentration is very important [11]. Transportation process of substrate from solution to electrode surface spread by the influence of the resistance, so electrode surface material concentration below solution substrate concentration, known as the concentration gradient. So this model assume that electronic transferring rely on the middle subject (including NADH and NADPH) from in cells to the cell surface, but this model does not include the part from in cells from cell surface, and while from cell wall to the electrode surface depends on the adding mediator thionine. Model use acetate as the substrate, the intermittent training mode.

2.2. Electrochemical reaction equation
2.2.1. Electrode reaction control equations
The process of mediator accepting and releasing electronic, using type (1) said:

$$M_{red} = M_{ox} + 2H^{+} + 2e^{-} \quad (1)$$

Type, M_{red} means reduced mediator, M_{ox} means oxidized mediator. A series of biochemical reaction process of substrate consumption and biomass growth of electrode surface and solution use double monod equationv [4] to describe, following formula (2) as shown. This formula applies both the electrode surface and solution.

$$\rho = q_{AC,\max} \times S_X \frac{S_{AC}}{k_{AC} + S_{AC}} \times \frac{S_{Mox}}{k_{Mox} + S_{Mox}}, \quad (2)$$

Parameters see table 1.

2.2.2. Current and quantity control equation
Ph for constant, the product current density use Butler-volmer equation [5], following formula (3) as shown.

$$i = i_{0,ref} \left(\frac{S_{E.Mred}}{S_{ref.Mred}}\right)\left(\frac{S_{E.Mox}}{S_{ref.Mox}}\right)^{-1}\left(\frac{S_{E.H}}{S_{ref.H}}\right)^{-2} \times \left[\exp\left(\frac{2.303}{b}\eta_{act}\right) - \exp\left(-\frac{2.303}{b}\eta_{act}\right)\right] \quad (3)$$

Local current density to the integral of the area called current formula (4) as shown.

$$I = \int_{A_F} \sum_j i_j \, dA \quad (4)$$

The production of charge is calculated by integral current for time formula (5) as shown.

$$Q = \int_0^t I \, dt \quad (5)$$

Parameters see Table 1.

Table 1. MFC Parameters

$S^0_{AC, B}$	Initial substrate concentration	*100(mg/L)*
$S^0_{Mred, B}$	Initial reduced mediator concentration	*10^{-3}(mM)*
$S^0_{Mox, B}$	Initial oxidized mediator concentration	*1(mM)*
$q_{AC, max}$	Maximum rate constant	*10(mg/L)*
$S^0_{X, B}$	Initial biomass concentration	*0.01or5(mg/L)*
$i_{0, ref}$	Reference current density	*2×10^{-4}(Am^{-2})*
$S_{ref, Mred}=S_{ref, Mox}$	Reference mediator concentration	*1(mM)*
$R_{int}+R_{ext}$	Total resistance	*1000（Ω）*
V_C	Cathode potential	*0.68（V）*
A_F	Anode area	*10^{-3}(m^2)*
K_{ac}	Acidity constant acetate	*100（mg/L）*
b	Tafel coefficient	*0.120（V）*
D_{AC}	Acetate diffusion coefficient	*6.5×10^{-6}*
$D_{Mred}=D_{Mox}$	Mediator diffusion coefficient	*2×10^{-6}*
Kmox	Haif-saturation coefficient	*0.1(mM)*
L_L	Boundary layer thickness	*10（μm）*
PH	PH	*7*
E^0_M	Mediator reduction potential	*0.477(V）*

2.2.3. Voltage and potential control equations

$$V_{cell} = E_{cell} - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad (6)$$

In formula, η_{act} means activation potential, η_{ohm} means ohms potential, η_{conc} means concentration potential. E means balance potential.

Ignore concentration potential losses, as the model use substrate concentration of electrode. Potential of cathode and anode is listed respectively. Formula (7) as shown.

$$V_{cell} = (E_C - \eta_{C,act}) - (E_A - \eta_{A,act}) - \eta_{ohm} \quad (7)$$

In MFC liquid exist internal resistance R_{int} , following ohm's law $\eta_{ohm} = IR_{\text{int}}$.

Because this mainly stuies the anode room, in order to simplify model, assuming cathode voltage is constant. Formula (8) as shown.

$$V_C = E_C - \eta_{C,act} \quad (8)$$

The balance of the anode reaction voltage E_A is about a function of standard redox potential, the revision is about redox mediator of the anode [2], written (9):

$$E_A = E^0_{Mox/Mred} + \frac{RT}{nF} \ln \frac{S_{Mox,E}}{S_{Mred,E}} S^2_{E,H^+} \quad (9)$$

By above get type (10), called a calculation formula of activation potential.

$$\eta_{A,act} = V_C - I(R_{\text{int}} + R_{ext}) - (E^0_{Mox/Mred} - 0.059PH + \frac{0.059}{2} \lg \frac{S^n_{Mox,E}}{S^n_{Mred,E}}) \quad (10)$$

3. Results and discussion

3.1. Simulation about different initial biomass concentration influencing biomass growth

In order to investigate different initial biomass evolution, this article simulated the process of solution and anode biomass growth in 25°C, initial substrate concentration for 100 mg/L, initial biomass rarely (MFC initial start-up phase) and initial biomass 5 mg/L, and the results of these simulation are as shown in Figure 1 and Figure 2 . Other initial conditions in simulation process see Table1.

From Figure 1, finding at MFC start-up phase, electrode biomass growth rate is much higher than the liquid biomass, and adhered to the electrode biomass is far greater than that liquid, biological growth accord with biological growth rule. In 0 to three days electrode biomass growth slow, in delay demurrage incurred, after 3 days biomass has a sharp increasing, into the logarithmic growth, and to the 8th days reaching to smoothly, into the stable and no longer growth. But the liquid biomass growth was significantly lower than the electrode biomass, because as biological catalystthe electrode is the electronic accepter of oxidation half response, can prompt electron transfer out, beneficial to the oxidation reactions happen, so as to facilitate the electrode surface microbial metabolism, makes the electrode surface biomass has increased dramatically. And electrode for biological provides also attached to the carrier, therefore, the electrode surface biomass significantly more than of liquid. Because the substrate constantly consumption, make electrodes biomass growth tending gradually smooth. At the same time, because of electrode surface biological fast growth, make a lot of substrate consumption in the electrode, the liquid biomass is restricted because there wasn't enough substrate, a slow growth trend, and with the substrate consumption, biomass ultimately no longer growth.

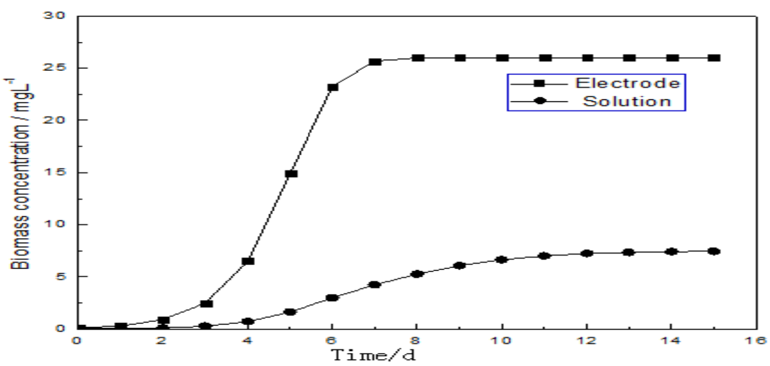

Figure 1. Initial Solution Biomass 0.01 mg/L, Solution Biomass and Biomass on Electrode Changing Over Time

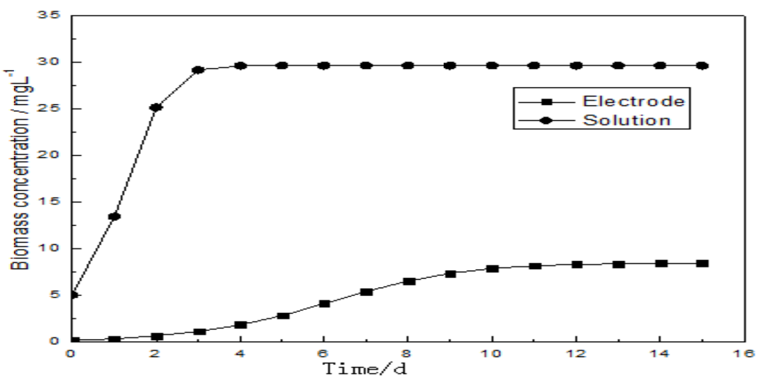

Figure 2. Initial Solution Biomass 5 mg/L, Solution Biomass and Biomass on Electrode Changing Over Time

From Figure 2 recover when initial biomass for 5 mg/L, solution biomass growth rate is much higher than the electrode growth rate, and the solution biomass growth dominant. Comparing with Figure 1 and Figure 2, initial biomass inoculating culture from the start, during in MFC reaction biomass growth is mainly the anode electrode surface; initial add more biomass to solution, biomass growth is in solution. The reason is that although MFC reaction stimulate the electrode surface microbial growth, but if initial solution biomass is the more, microbial on the electrode growth need time, suspended microbes in the solution is at first consumption substrate, biomass in solution would go to growth, substrate will be in solution consumption, when substrate is fewer gradually, in solution biomass growth is balanced, almost no longer grow, because electrode microbial consumption substrate was floating in the solution of microorganism restrictions, so on electrodes biomass slowly increase, biomass continue to grow on electrode until the substrate is exhausted.

3.2. Simulation about different initial biomass concentration influencing producing electricity

In order to research different initial biomass effect MFC producing electrical performance, this article simulate current and electric charge for 25°C, the initial substrate concentration for 100 mg/L, initial biomass rarely (MFC initial start-up phase) and initial biomass 5 mg/L. The simulation results are as shown in figure 3 and in figure 4. Simulation process other initial conditions see Table 1.

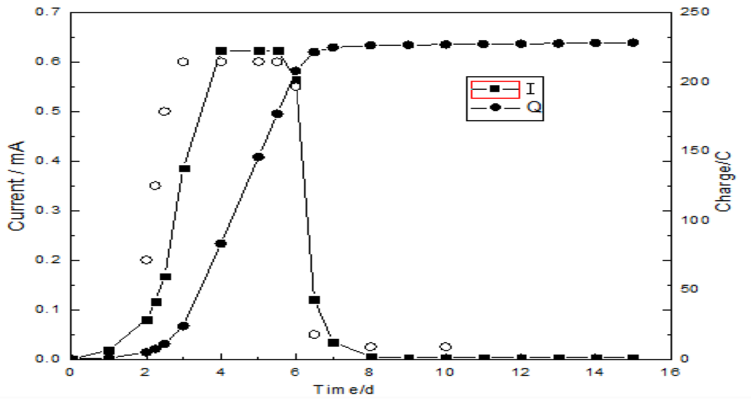

Figure 3. Initial Solution Biomass0.01mg/l, Current and Charge Changing Over Time Hollow Circle is li Haoran's Experiment

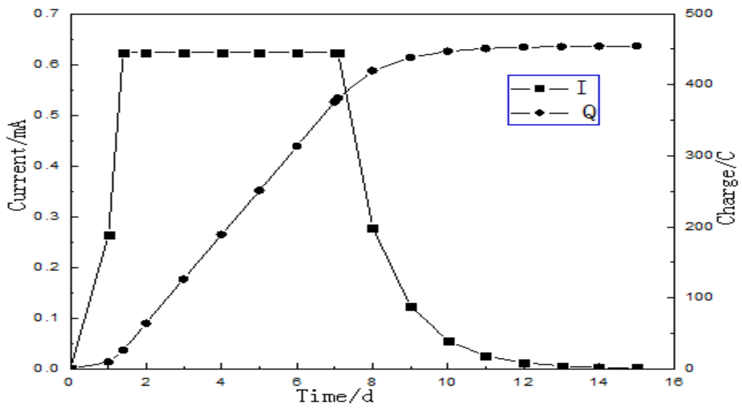

Figure 4. Initial Solution Biomass 5mg/L, Current and Charge Changing Over Time

Through the Figure 3 and Figure 4 finding the bigger initial added to the solution biomass, the fast the current to reach the maximum, the longer current in maximum maintain, the more the charge. In figure 3 current just began to slow growth, rapid growth to maximum, keep a period of time before the fall [7], in Figure 3 hollow circle as shown. Because the initial biomass is of little, as shown in figure 1 shows initial biomass growth slow, lead to just begin to consume less of substrate, producing electronic is little, the first current is small. Figure 1 biomass as time accumulated ceaselessly, so the rate of generating electron will be faster, appeared as shown in Figure 3 current growth. Figure 4 current in a short period of time to achieve maximum. Reason can be seen from the chart 2, when the initial biomass for 5.00 mg/L, solution biomass in a rapidly growing and in a short time biomass breeding reaching a maximum. Biomass consume substrate produce electronic, generated current rapid reach a maximum. Figure 3 and Figure 4 the maximum current is same, the reason is that mediator is a chemical substance to bring electron from cell walls to the electrode surface, oxidized mediator in cell accept electron into reduced mediator, reduced mediator release the electronic to the anode electrode surface, after that become oxidized mediator to the cell surface, the cycle form generate current, in the MFC process transferring electron mainly rely on mediator releasing electron to the electrode surface, because of the initial fixed mediator, so Figure 3 and Figure 4 the maximum current almost is the same. In Figure 4 current maximum continuous last time long time than in Figure 3, reason is initial more biomass reproduce rapidly at began producing a considerable amount of electronics, a large number of electronic must depend on mediator transferring to the electrode surface, with fixed mediator, producing current time will last, it makes current in a period of time maintaining the maximum. In Figure 4 and Figure 5 get vaccinated some biomass in MFC initial stage benefit produce electricity.

Figure 1 and Figure 3 can also explain when the initial added to the solution biomass were very small, to produce electricity the main function biomass is on electrode [6] and others experimental proof from the start of training, the creation of electric power is mainly attributed to biomass of the electrode. Figure 2 and Figure 4 shows the initial add more biomass to MFC solution, to produce electricity the main function biomass is in solution.

3.3. Simulation about different initial biomass concentration influencing substrate degradation

In order to study different initial biomass concentration to substrate degradation, this section simulate the substrate degradation, for the initial biomass concentration respectively rarely (MFC initial start-up phase) and 5.00mg/L, other conditions remain unchanged, the simulation results as shown in figure 5.

The figure 5 the bigger initial biomass concentration, the faster substrate degradation rate, the faster substrate consumed [8] experiment conclusion is in agreement that anode biomass reduce, COD removal rate reduce. As shown in figure 5 when the initial solution biomass very little, at the beginning three days degradation slowly, with time, the substrate concentration began to decrease abruptly, in 6 days the substrate decomposition rate was reduced, until 13 days the substrate consumed.

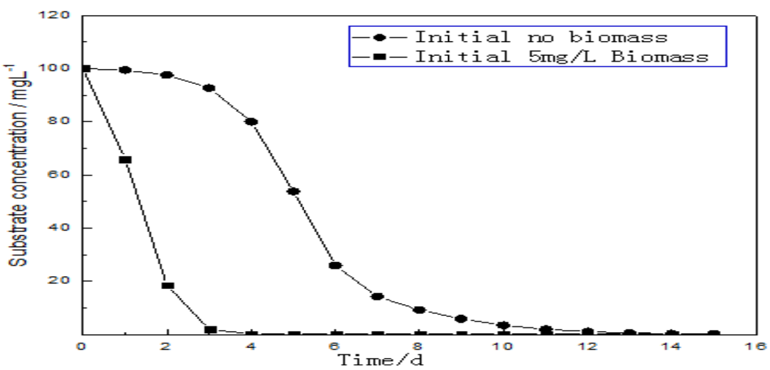

Figure 5. Initial Solution Biomass 0.01 mg/L and 5 mg/L, Substrate Concentration Changing Over Times

As shown in figure when the initial biomass concentration is very big, the substrate in the beginning is quickly degradated, in about four days is consumed. This is because when biomass concentration is very small, biomass consumption substrate ability is limited, the substrate degradation is slow, substrate experience slow degradation, rapid degradation and exhausted. When the initial biomass is very big, the figure 2 shows solution biomass rapid growth, a large number of biomass growing to breed accelerated the consumption of substrate, and soon the substrate consumed. The substrate degradation law is accord with biomass growth law, that is, the initial stage in biological delay demurrage incurred stage, biomass less, substrate degradation slow, when creatures into the logarithm , the substrate consumption also rapidly increase, when creatures into the stable, the substrate is basic consumed.

3.4. Simulation about different initial biomass concentration influencing mediator

In order to study different initial biomass concentration effecting mediator, this section simulate mediator variations, for in 25°C, initial substrate concentration for 100 mg/L, initial mediator concentration for 1 mmol/L, initial biomass rarely (MFC initial start-up phase) and initial biomass 5 mg/L. Simulation results are as shown in figure 6 and figure 7. Other initial conditions in simulation process to see table 1.

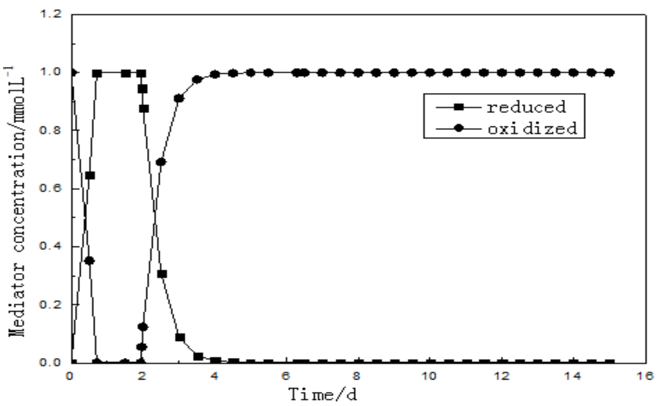

Figure 6. Initial Solution Biomass 0.01mg/L, Mediator Changing Over Times

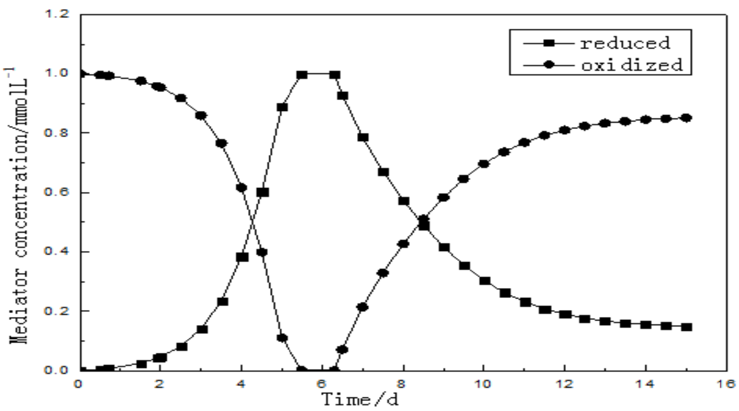

Figure 7. Initial Solution Biomass 5 mg/L, Mediator Changing Over Times

The figure 6 and figure 7, it is known that the more initial biomass, the faster mediator change, the first shorter mediator to maximum. As shown in figure 6 shows when the initial biomass has rarely, mediator changes in the first two days slowly, as time, oxidized mediator began to rapidly decreases, and also reduced mediator began to increase quickly, and maintain a few days on the maximum, oxidized mediator and reduced mediator began to rise and fall, respectively. As shown in figure 7 shows, when the initial biomass for 5 mg/L, at first mediator will be change rapidly, oxidized mediator fell rapidly, reduced mediator rising rapidly, and achieve maximal can change after a few days the scope of maintaining, oxidation state and also after Yuan Tai began to rise and fall, respectively. Because the more initial biomass the quicker substrate consume, the sooner this will produce electronic, the faster oxidized mediator become reduced mediator, when reduced mediator getting to 1 mmol/L, as the microbial continue to consume substrate producing electronic, reduced mediator remain maintain in a period of time until generating electron not make reduced mediator in maximum, oxidized mediator began to increase, reduced mediator began to decrease.

4. Conclusion

The solution initial biomass has almost no, MFC microorganism grow mainly on the electrode surface, in solution microbial growth is small; The solution with a larger initial biomass, microbial growth breeding mainly in solution , the electrode surface biomass grow slowly. The bigger the solution initial biomass,the fast the current to reach the maximum, the longer current maintain maximum time , the more the charge ; the mediator amount is certain, the maximum current almost unchanged. The solution initial biomass has almost no, current comes from electron generated from the electrode surface biomass consuming substrate ; The initial solution has a larger biomass, current comes from electron generated from solution biomass consuming substrate. The more the initial solution suspension biomass, the fast mediator change.

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