

Modelisation and Optimization of a Microbial Desalination Cell System

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Abstract

In this work, we used a hybrid system composed of a Microbial Desalination Cell (MDC). This system allows, at the same time, the treatment of wastewater and the production of electrical energy for the desalination of saltwater. MDC is a cleaning technology used to purify wastewater. This process has been driven by converting organic compounds contained in wastewater into electrical energy through biological, chemical, and electrochemical processes. The produced electrical energy was used to desalinate the saline water. The objective of this work is the desalination or pre-desalination of seawater. For this, we have established a theoretical model consisting of differential equations describing the behavior of this system. Subsequently, we developed a program on MATLAB software to simulate and optimized the operation of this system and to promote the production of electrical energy in order to improve the desalination efficiency of the MDC. The theoretical result shows that the electrical current production is maximal when the methanogenic growth rate equal to zero, increases with the increasing of influent substrate concentration and the efficiency of desalination increased with flow rate of saline water.

Keywords

Microbial Desalination Cell, Desalination, Wastewater, Electrical Current Production

1. Introduction

With rapid population growth, economic development, the demand for safe freshwater increased considerably [1]. More than one-third of the world's population lives in water-stressed countries, this situation is predicted to increase to nearly two-thirds in 2025 [2]. Desalination of brackish water and seawater has been used to produce potable water in many parts of the world, but most water desalination

technologies are considered energetic and costly [3]. Traditional desalination processes currently used are reverse osmosis, solar desalination, electrodialysis, thermal desalination, etc. Traditional desalination processes currently used are reverse osmosis, solar desalination, electrodialysis, thermal desalination, etc. Since the high energy requirements of these technologies constitute a major challenge, it is important to develop techniques for the desalination of seawater and brackish water powered by renewable energies [4].

Bioelectrochemical Systems (BES) are emerging and promising concepts in energy recovery and wastewater treatment, that apply microorganisms to convert chemical energy present in wastewater to electrical energy through various reactions [5] [6] [7] [8]. BES is studied with different configurations and designs, including microbial fuel cells, microbial electrolysis cells and microbial desalination cells [6] [9] [10] [11] [12].

MDC is a recent and potential method of brackish water desalination. This innovative technology can concurrently treat wastewater and generate electrical energy from wastewater without using external electricity [13].

A typical MDC consists of three chambers, an anode, middle, and a cathode, separated by an Anion Exchange Membrane (AEM, between the anode and the middle chambers) and a Cation Exchange Membrane (CEM, between the cathode and the middle chambers), respectively.

The anode is responsible for electricity production by the degradation of organic matter containing in the wastewater, in the middle chamber the salt remove from saline water. In this process, the anions (Cl^-) move across the AEM to the anode chamber and the cations (Na^+) migrate across the CEM to the cathode chamber, whereas the cathode completes the electrical circle [14].

Through mathematical modeling tools, we can better understand the MDC process, analyze it, and demonstrate the feasibility of this technology both for the production of freshwater with low energy consumption and the treatment of wastewater.

The use of mathematical models will provide an analytical description that might convert complex systematic phenomena into simple series of mathematical expressions to describe the effect of every component on the overall output [15] [16].

In this study, differential equations are used as main mathematical equations combined biological, physical, chemical, and electrochemical principles to solve specific problems.

A multiplicity of studies has been conducted to study the performance of MDC who is affected by biological, electrochemical and physical aspects (microbial community, configurations, etc.) [17] [18] [19] and considerable works have been conducted to optimize the above aspects [5] [9] [10] [19] [20] [21].

Reduction in energy production due to loss of substrate consumed by methanogens makes methanogenesis a serious limitation in the performance of Microbial Fuel Cells (MFCs) [22].

Many authors have examined methanogen activity in microbial fuel cells when

exposed to various environmental stresses, such as oxygen, low pH, low temperature, and the addition of methanogenesis inhibitors.

Somdipta, B. and Manaswini, B. [22] observed that Aluminum (Al) due to its antibacterial properties easily affects methanogens (Gram⁺), which have a thinner cell membrane, therefore, more sensitive to Al and a growth rate slower. Whereas, Gram⁻ exoelectrogens have a thick cell membrane, thus remaining unaffected.

Chae *et al.* [23] concluded that a BES (2-bromoethanesulfonate) injection to the anode chamber was the most effective strategy for the selective inhibition of methanogens without damaging exoelectrogens which will increase the production of electricity and decrease the methane production in MFCs. Therefore, the kinetic parameters of electricigenic microorganisms were estimated using this data set by setting the methanogenic growth rate to zero.

2. Description of the Microbial Desalination Cell

As shown in **Figure 1**, the MDC unit consists of three chambers an anode, middle (water to be desalinated), a cathode, separated by an Anion Exchange Membrane (AEM) next to the anode and a Cation Exchange Membrane (CEM) by the cathode [24]. At the anode chamber, bacteria consume and oxidize organic matters containing in waste water and form an aggregate cell known as biofilm [25] [26]. This biofilm adheres to the anode surface and initiates the process of bio-catalysis to release protons and electrons [27].

The electrons produced from cell respiration move from the anode to the cathode through an external circuit that links the two electrodes and create an electrical field that separates salts in saline water [28].

At the cathode chamber, O₂ uses the electrons from the external circuit to undergo reduction and produce pure water. This causes a potential gradient across the anode and cathode chambers. Therefore, to maintain electroneutrality, the anions (Cl⁻) flow across the AEM from the salt water in the middle chamber in to the anode, while the cations (Na⁺) migrate to the cathode chamber across the CEM [14].

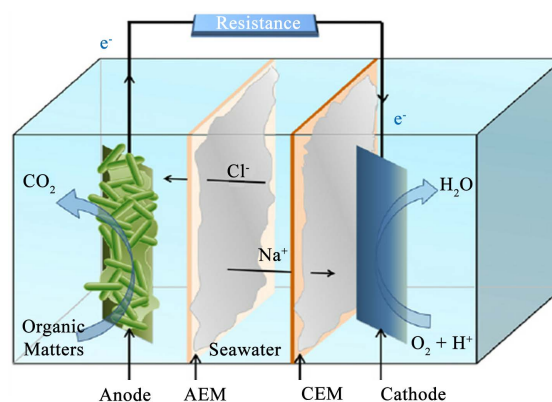
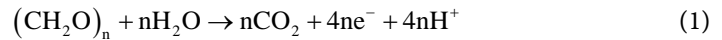


Figure 1. Typical scheme of microbial desalination cell [29].

The equations of the anode and the cathode reactions are given, respectively, by:



3. MDC Modeling and Electrical Current Generation

Mathematical models are used to convert complex phenomena into simple mathematical expressions and to describe the effect of each component on the overall output [15] [30]. The major equations are combined with chemical, electrochemical and physical, principles to resolve specific problems.

3.1. MDC Modeling

3.1.1. Mass Balances for Substrate and Microorganisms in the Anode

Differential equations could be used to quantify the concentrations of the substrate and microorganisms (anodophilic and methanogenic) in the anode compartment. These differential equations were based on or modified from the study [31].

The mass balance for the substrate is shown in Equation (3):

$$\frac{dS}{dt} = D_{anode} * (S_{in} - S) - k_{s,a,max} \frac{SM_{OX}}{K_a + SK_M + M_{OX}} * C_a - k_{s,m,max} \frac{S}{K_m + S} * C_m \quad (3)$$

where:

- S : Concentration of the substrate which is the wastewater for this work ($\text{mg}_S \cdot \text{l}^{-1}$);
- S_{in} : Concentration of the influent substrate ($\text{mg}_S \cdot \text{l}^{-1}$);
- C_a and C_m : Concentrations of anodophilic and methanogenic microorganisms ($\text{mg}_C \cdot \text{l}^{-1}$), respectively;
- $k_{s,a,max}$ and $k_{s,m,max}$: Maximum substrate consumption rates by anodophilic and methanogenic microorganisms ($\text{mg}_S \cdot \text{mg}_a^{-1} \cdot \text{day}^{-1}$), respectively;
- M_{OX} : Oxidized mediator fraction per anodophilic microorganism ($\text{mg}_M \cdot \text{mg}_a^{-1}$);
- K_a , K_m , and K_M : The half-saturation concentrations for the anodophilic microorganisms, methanogenic microorganisms, and the redox mediator ($\text{mg}_S \cdot \text{l}^{-1}$, $\text{mg}_S \cdot \text{l}^{-1}$, and $\text{mg}_M \cdot \text{mg}_a^{-1}$), respectively.
- D_{anode} : The dilution rate (day^{-1}) as defined by the below equation:

$$D_{anode} = \frac{Q_{in}}{V_{anode}} \quad (4)$$

where:

- Q_{in} : Influent flow rate of the substrate ($\text{l} \cdot \text{day}^{-1}$);
- V_{anode} : Volume of the anode compartment (l);

Differential equation for the anodophilic microorganism's concentration in the anode compartment is shown in Equation (5):

$$\frac{dC_a}{dt} = k_a C_a - k_{d,a} C_a - D_{anode} \frac{1 + \tanh\left(k_{a,x} (C_a + C_m - C_{a,max})\right)}{2} C_a \quad (5)$$

Differential equation for the methanogenic microorganism's concentration in the anode compartment is shown in Equation (6):

$$\frac{dC_m}{dt} = k_m C_m - k_{d,m} C_m - D_{anode} \frac{1 + \tanh\left(k_{m,x} (C_a + C_m - C_{m,max})\right)}{2} C_m \quad (6)$$

where:

- $k_{d,a}$ and $k_{d,m}$: Decay rates of the microorganisms (day^{-1});
- $k_{a,x}$ and $k_{m,x}$: Steepness factors for anodophilic microorganism ($\text{l}\cdot\text{mg}_a^{-1}$) and methanogenic microorganisms ($\text{l}\cdot\text{mg}_m^{-1}$) for the biofilm retention;
- $C_{a,max}$ and $C_{m,max}$: The maximum attainable concentrations for anodophilic and methanogenic microorganisms ($\text{mg}_m\cdot\text{l}^{-1}$);
- k_a and k_m : Growth rates of the microorganisms (day^{-1}) calculated by the Equations (7) and (8):

$$k_a = k_{a,max} \frac{SM_{ox}}{K_a + SK_M + M_{ox}} \quad (7)$$

$$k_m = k_{m,max} \frac{S}{K_m + S} \quad (8)$$

where:

- $k_{a,max}$ and $k_{m,max}$: The maximum microorganism growth rates (day^{-1}).

The intracellular material balance for the oxidized mediator can be shown below:

$$\frac{dM_{OX}}{dt} = -Y_M k_{s,a} + \frac{\gamma I_{MDC}}{V_{anode} C_a n_e F} \quad (9)$$

$$M_{total} = M_{OX} + M_{red} \quad (10)$$

where:

- M_{total} : Total mediator fraction per microorganisms ($\text{mg}_M\cdot\text{mg}_a^{-1}$);
- M_{red} : Reduced mediator fraction per microorganisms ($\text{mg}_M\cdot\text{mg}_a^{-1}$);
- Y_M : Stands for the mediator yield ($\text{mg}_M\cdot\text{mg}_S^{-1}$);
- γ : Mediator molar mass ($\text{mg}_M\cdot\text{mole}_M^{-1}$);
- I_{MDC} : Current through the circuit of MDC (A);
- F : Faraday constant = 96,485 A. s. mole^{-1} ;
- n_e : number of electrons transferred per mole of mediator ($\text{mole}_e\cdot\text{mole}_M^{-1}$).

3.1.2. Mass Balance of Salt

Ordinary differential equations shown below are developed to quantify the salt concentration during the desalination process:

$$\frac{dC_{salt,m}}{dt} = D_{salt} * (C_{salt,in} - C_{salt,m}) - d * (C_{salt,m} - C_{salt,a}) - d * (C_{salt,m} - C_{salt,c}) - I_{MDC} / F * V_{salt} \quad (11)$$

$$\frac{dC_{salt,a}}{dt} = d * (C_{salt,m} - C_{salt,a}) - D_{anode} * C_{salt,a} \quad (12)$$

$$\frac{dC_{salt,c}}{dt} = d * (C_{salt,m} - C_{salt,c}) \quad (13)$$

where:

- $C_{salt,m}$, $C_{salt,a}$ and $C_{salt,c}$: Concentrations of salt in desalination, anode and cathode compartments ($\text{mg}\cdot\text{l}^{-1}$) respectively;
- D_{salt} : dilution rate (day^{-1}) in the salt compartment (the ratio of the salt flow rate (Q_{salt}) over the volume of the salt compartment (V_{salt}));
- d : membrane salt transfer coefficient (is the ratio between the product of diffusion coefficient and membrane surface area and the product of the membrane thickness and the anode volume (day^{-1})).

3.2. Electrical Current Generation

The MDC current is calculated as:

$$OP_{conc} = \frac{RT}{F} \ln \left(\frac{M_{total}}{M_{red}} \right) \quad (14)$$

$$I_{MDC} = \frac{V_{oc} - OP_{conc}}{R_{ext} + R_{int}} \quad (15)$$

- OP_{conc} : Overpotential concentration (v);
- R_{int} : Internal resistance of MDC (defined by [32]);
- R_{ext} : External resistance (Ω);
- V_{oc} : Open circuit Voltage (v).

According to the previous studies [31] the open circuit potential of the MDC used in the model was equal to 1.2 V.

The parameters values used in the present study are shown in **Table 1** and **Table 2**.

4. Results and Discussion

The relationship between the current production and methanogenic growth rate is shown in **Figure 2**.

Table 1. Parameters values used in this study.

Parameters	Description	Values
V_{salt}	Volume of the desalination compartment	150 l
V_{anode}	Volume of the anode compartment	300 l
$V_{cathode}$	Volume of the cathode compartment	300 l
F	Faraday constant	1.116 A·day·mol ⁻¹
d	Salt transfer capacity of the membrane	0.029 mole·l ⁻¹ ·day ⁻¹
R	Ideal gas constant	0.08206 l·atm·K ⁻¹ ·mol ⁻¹
T	Cell temperature	298.15 K
R_{ext}	External resistance	0.1 Ω

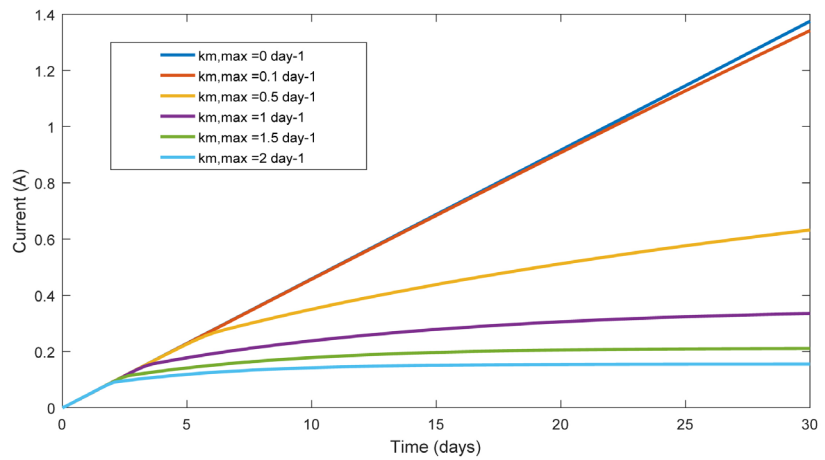


Figure 2. The current production vs. time for different methanogenic growth rate values (The influent substrate concentration $S_{in} = 1000 \text{ mg}_S \cdot \text{l}^{-1}$).

Table 2. Parameters values used in the mathematical model [31].

Parameters	Description	Values
$k_{s,a,max}$	Maximum substrate consumption rates by anodophilic microorganisms	$5.32 \text{ mg}_S \cdot \text{mg}_a^{-1} \cdot \text{day}^{-1}$
$K_{s,m,max}$	Maximum substrate consumption rates by methanogenic microorganisms	$8.20 \text{ mg}_S \cdot \text{mg}_a^{-1} \cdot \text{day}^{-1}$
K_a	The half-saturation concentration for the anodophilic microorganisms	$20 \text{ mg}_S \cdot \text{l}^{-1}$
K_m	The half-saturation concentration for the methanogenic microorganisms	$80 \text{ mg}_S \cdot \text{l}^{-1}$
K_M	The half-saturation concentration for the redox mediator	$0.2 * M_{total} \text{ mg}_M \cdot \text{mg}_a^{-1}$
$K_{a,x}$	The steepness factors for anodophilic microorganism	$0.04 \text{ l} \cdot \text{mg}_a^{-1}$
$K_{m,x}$	The steepness factors for methanogenic microorganisms	$0.04 \text{ l} \cdot \text{mg}_m^{-1}$
$C_{a,max}$	The maximum attainable concentrations for anodophilic microorganisms	$512.5 \text{ mg}_a \cdot \text{l}^{-1}$
$C_{m,max}$	The maximum attainable concentrations for methanogenic microorganisms	$525 \text{ mg}_m \cdot \text{l}^{-1}$
$K_{a,max}$	The maximum microorganism growth rate for anodophilic microorganisms	0.197 day^{-1}
$K_{m,max}$	The maximum microorganism growth rate for methanogenic microorganisms	0.1 day^{-1}
M_{total}	Total mediator fraction per microorganisms	$0.05 \text{ mg}_M \cdot \text{mg}_a^{-1}$
Y_M	The mediator yield	$6.14 \text{ mg}_M \cdot \text{mg}_S^{-1}$
γ	Mediator molar mass	$663,400 \text{ mg}_M \cdot \text{mole}_M^{-1}$
n_e	The number of electrons transferred per mole of mediator	$2 \text{ mole}_e \cdot \text{mole}_M^{-1}$

Figure 2 shows that the current production increased with the decreasing of methanogenic growth rates. The result confirms that the maximum electrical production is reached if the growth rate of the methanogenic population is equal to

zero (only the electricigenic population exists).

For various values of the influent substrate concentration the simulation result of current generation is shown in **Figure 3**.

Figure 3 shows that where methanogens have zero growth, the electrical current increases with the increasing of influent substrate concentration. In a period of 30 days the maximum current reached 1.4 A when the influent substrate concentration is more than 1000 mg/l.

The effect of varying salt solution flow rates on the change of the salt concentration in the middle compartment is shown in **Figure 4**. When the flow rate of saline water decreased, salt removal is more important. The salt concentration decreased significantly from initial 35 g/l to around 7 g/l when the salt solution flow rate is less than or equal to 0.1 l/day.

Figure 5 shows that the salt concentration in the middle compartment decreased with the time for different initial salt concentrations. The final salt concentration responded to the variation of initial salt concentration.

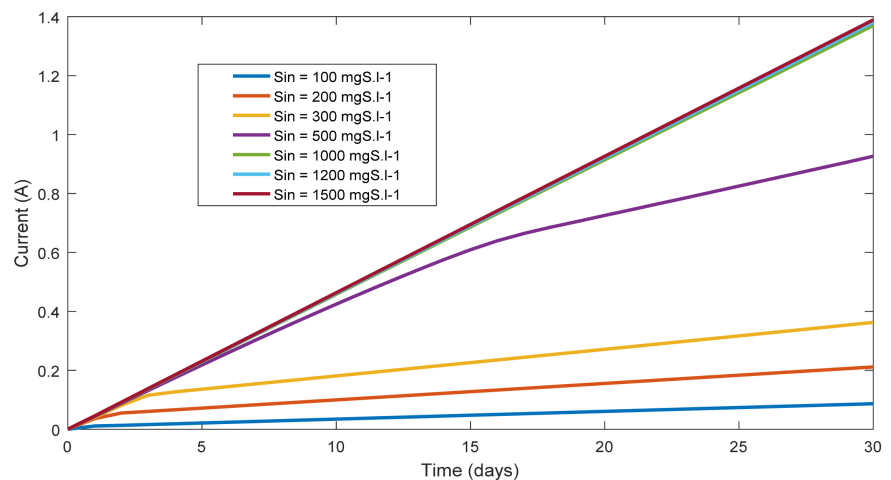


Figure 3. The current production vs. time for different influent substrate concentration values (the methanogenic growth rate $k_{m,max} = 0$).

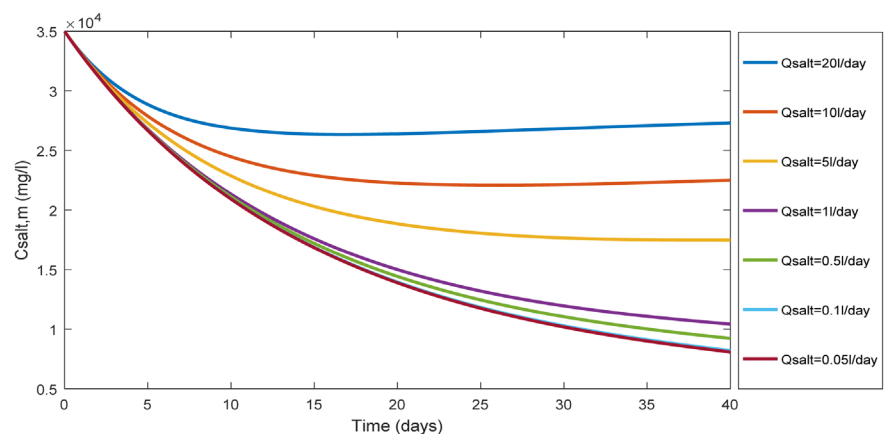


Figure 4. The salt concentration in the desalination compartment vs. time for different salt solution flow rates.

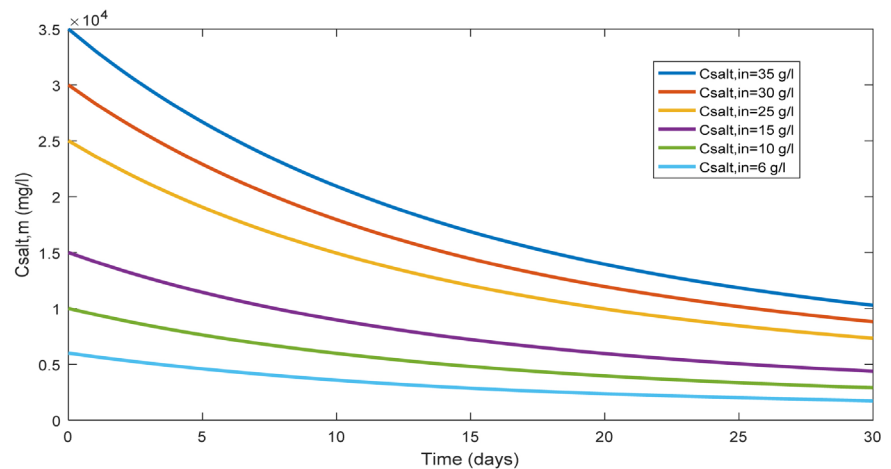


Figure 5. The salt concentration in the desalination compartment vs. time for different initial salt concentrations (when $Q_{salt} = 0.1$ l/day).

5. Conclusions

The Microbial Desalination Cell (MDC) is an emerging and promising technique or concept for simultaneous wastewater treatment and water desalination. The principle of this technology is to use electricity generated by the bacteria existing in wastewater and create an electrical field that separates salts in saline water. In this study, a mathematical modeling and simulation study of a microbial desalination cell was performed using the MATLAB software program.

The results obtained allowed us to show that the developed program in this study will be a useful tool for the optimization of the operation of this system and to promote the production of electrical energy in order to improve the desalination efficiency by MDC.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Nomenclature

- MDC: Microbial Desalination Cell
- AEM: Anion Exchange Membrane
- CEM: Cation Exchange Membrane
- V_{oc} : Open circuit Voltage (v)
- OP_{conc} : Overpotential concentration (v)
- R_{int} : Internal resistance of MDC (Ω)
- R_{ext} : External resistance (Ω)
- $C_{salt,m}$: Concentrations of salt in desalination compartment ($\text{mg}\cdot\text{l}^{-1}$)
- $C_{salt,a}$: Concentrations of salt in anode compartment ($\text{mg}\cdot\text{l}^{-1}$)
- $C_{salt,c}$: Concentrations of salt in cathode compartment ($\text{mg}\cdot\text{l}^{-1}$)
- Q_{salt} : Flow rate of the salt solution in the desalination compartment ($\text{l}\cdot\text{day}^{-1}$)
- Q_{anode} : Flow rate of anolyte in the anode compartment ($\text{l}\cdot\text{day}^{-1}$)
- V_{salt} : Volume of the desalination compartment
- V_{anode} : Volume of the anode compartment
- $V_{cathode}$: Volume of the cathode compartment
- $C_{salt,in}$: Salt concentration in the salt influent ($\text{mg}\cdot\text{l}^{-1}$)
- D_{salt} : Dilution rate in the desalination compartment (day^{-1})
- D_{anode} : Dilution rate in the anode compartment (day^{-1})
- d : membrane salt transfer coefficient (day^{-1})
- S : Concentration of the substrate (waste water in this work) ($\text{mg}_S\cdot\text{l}^{-1}$)
- S_{in} : Concentration of the influent substrate ($\text{mg}_S\cdot\text{l}^{-1}$)
- C_a and C_m : Concentrations of anodophilic and methanogenic microorganisms ($\text{mg}_C\cdot\text{l}^{-1}$), respectively
- $k_{s,a,max}$ and $k_{s,m,max}$: Maximum substrate consumption rates by anodophilic and methanogenic microorganisms ($\text{mg}_S\cdot\text{mg}_a^{-1}\cdot\text{day}^{-1}$), respectively
- M_{OX} : Oxidized mediator fraction per anodophilic microorganism ($\text{mg}_M\cdot\text{mg}_a^{-1}$)
- K_a , K_m , and K_M : The half-saturation concentrations for the anodophilic microorganisms, methanogenic microorganisms, and the redox mediator ($\text{mg}_S\cdot\text{l}^{-1}$, $\text{mg}_S\cdot\text{l}^{-1}$, and $\text{mg}_M\cdot\text{mg}_a^{-1}$), respectively
- Q_{in} : Influent flow rate of the substrate ($\text{l}\cdot\text{day}^{-1}$)
- $k_{d,a}$ and $k_{d,m}$: Decay rates of the microorganisms (day^{-1})
- $k_{a,x}$ and $k_{m,x}$: Steepness factors for anodophilic microorganism ($\text{l}\cdot\text{mg}_a^{-1}$) and methanogenic microorganisms ($\text{l}\cdot\text{mg}_m^{-1}$) for the biofilm retention
- $C_{a,max}$ and $C_{m,max}$: The maximum attainable concentrations for anodophilic and methanogenic microorganisms ($\text{mg}_m\cdot\text{l}^{-1}$)
- k_a and k_m : Growth rates of the microorganisms (day^{-1})
- $k_{a,max}$ and $k_{m,max}$: The maximum microorganism growth rates (day^{-1})
- M_{total} : Total mediator fraction per microorganisms ($\text{mg}_M\cdot\text{mg}_a^{-1}$)
- M_{red} : Reduced mediator fraction per microorganisms ($\text{mg}_M\cdot\text{mg}_a^{-1}$)
- Y_M : Stands for the mediator yield ($\text{mg}_M\cdot\text{mg}_S^{-1}$)
- γ : Mediator molar mass ($\text{mg}_M\cdot\text{mole}_M^{-1}$)
- I_{MDC} : Current through the circuit of MDC (A)

- F : Faraday constant ($\text{A}\cdot\text{day}\cdot\text{mole}^{-1}$)
- n_e : number of electrons transferred per mole of mediator ($\text{mole}_e\cdot\text{mole}_M^{-1}$)