



## A high-performance photo-microbial desalination cell



Yuxiang Liang<sup>a,b</sup>, Huajun Feng<sup>a,b,\*</sup>, Dongsheng Shen<sup>a,b</sup>, Na Li<sup>a,b</sup>, Yuyang Long<sup>a,b</sup>,  
Yuyang Zhou<sup>a,b</sup>, Yuan Gu<sup>a</sup>, Xianbin Ying<sup>a</sup>, Qizhou Dai<sup>c</sup>

<sup>a</sup> School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

<sup>b</sup> Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling, Hangzhou 310012, China

<sup>c</sup> College of Environment, Zhejiang University of Technology, Hangzhou 310032, China

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### ABSTRACT

This paper introduces a high-performance photo-microbial desalination cell (PMDC) based on photo-electrochemical interactions. The anode of the cell was successfully modified with nanostructured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The maximum current density of the PMDC during operation was 8.8 A m<sup>-2</sup> at an initial salt concentration of 20 g L<sup>-1</sup>, which was twice that of the unmodified microbial desalination cell. The results of electrochemical impedance spectroscopy and cyclic voltammetry indicated the current increase of PMDC was mainly contributed by the high electron transfer rate at electrode/biofilm interface. The salt concentration of the effluent from the middle chamber was below ca. 1.4 mg L<sup>-1</sup> and the salt removal performance of the PMDC was always higher than 96%. The calculated number of harvested electrons agreed well with NaCl removal. In conclusion, the present PMDC effectively offers simultaneous electricity generation and desalination.

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### 1. Introduction

Freshwater scarcity [1] and energy shortages [2] are the main dilemmas for most small-sized islands. In the last few decades, enormous efforts have been focused on the supply of both freshwater and energy from renewable sources. At present, numerous typical desalination technologies have been commercialized such as reverse osmosis filtration system, electroosmosis and multiple-effect evaporation [3,4]. However, such desalination technologies running at the expense of massive energy consumption are not sustainable.

A new desalination method named microbial desalination cell (MDC) was invented in 2009 [5], which was an emerging desalination technology that offers simultaneous wastewater treatment, electricity generation, and desalination [6]. Compared with traditional distillation, MDC provided a more energy-efficient and eco-friendly option for desalination [7] through using microbes as catalysts to drive oxidation reactions in order to convert organic waste into electricity [8]. However, MDC technology today appears to be constrained by low desalination efficiency, mainly resulting from the low current density. For

example, Mehanna et al. [9] reported a microbial electro dialysis cell for water desalination and hydrogen gas production, while the removal ratio was just 37% due to the low current (2 A m<sup>-2</sup>). Jacobson et al [10], used a continuously operated upflow microbial desalination cell with an air cathode, but this system only produced a low current density of 0.7 A m<sup>-2</sup> which was difficult to achieve standard desalting effect (<20%). In addition, there have been a lot of similar reports with low desalination efficiency (<80%). Therefore, the improvement of current densities to achieve better desalination performance is an extremely urgent research topic.

The electricity generating mechanism of MDC is similar to that of microbial fuel cell (MFC) which the current is generated by using microbes on anode as catalysts to drive oxidation reactions. At present, a large amount of anodic surface modifications such as heat treatment, electrochemical oxidation, carbon nanotube coating has been successful in increasing the current densities in MFC [11–14]. Therefore, anodic surface modification is available for increasing the current densities of MDC likewise.

Recently bio-photoelectrochemical cells have attracted great interest as a new way to increase the power output of microbial fuel cells by exploiting sunlight as a driver without increasing operational cost. For example, hematite nanowire photoanodes for high-performance microbial fuel cells [15], nanowire-bacteria hybrids for unassisted solar carbon dioxide fixation [16], and nanowire photocathodes for solar-driven microbial

\* Corresponding author at: School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China Tel.: +86 571 87397126; fax: +86 571 87397126.

E-mail address: [Fenghuajun@mail.zjgsu.edu.cn](mailto:Fenghuajun@mail.zjgsu.edu.cn) (H. Feng).

photoelectrochemical cells [17] have been reported. Therefore, it would be attractive to combine an MDC with a bio-photoelectrochemical cell to obtain a high-performance photo-microbial desalination cell (PMDC).

Herein, we aimed to design a new composite bio-photocatalyst anode (PBA) and PMDC. Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), as a promising photocatalyst, has attracted considerable attention owing to its small band gap (2.2 eV), which is favorable for the efficient absorption of energy in the ultraviolet and visible light regions [18]. Thus, nanostructured  $\alpha\text{-Fe}_2\text{O}_3$  was chosen as the photocatalyst for the PMDC. Graphite was chosen as the anode carrier because of its excellent biocompatibility [19]. The current generation and desalination efficiency of the PBDC were used to evaluate its capacity.

## 2. Experimental

### 2.1. Synthesis of bio-photocatalyst anode

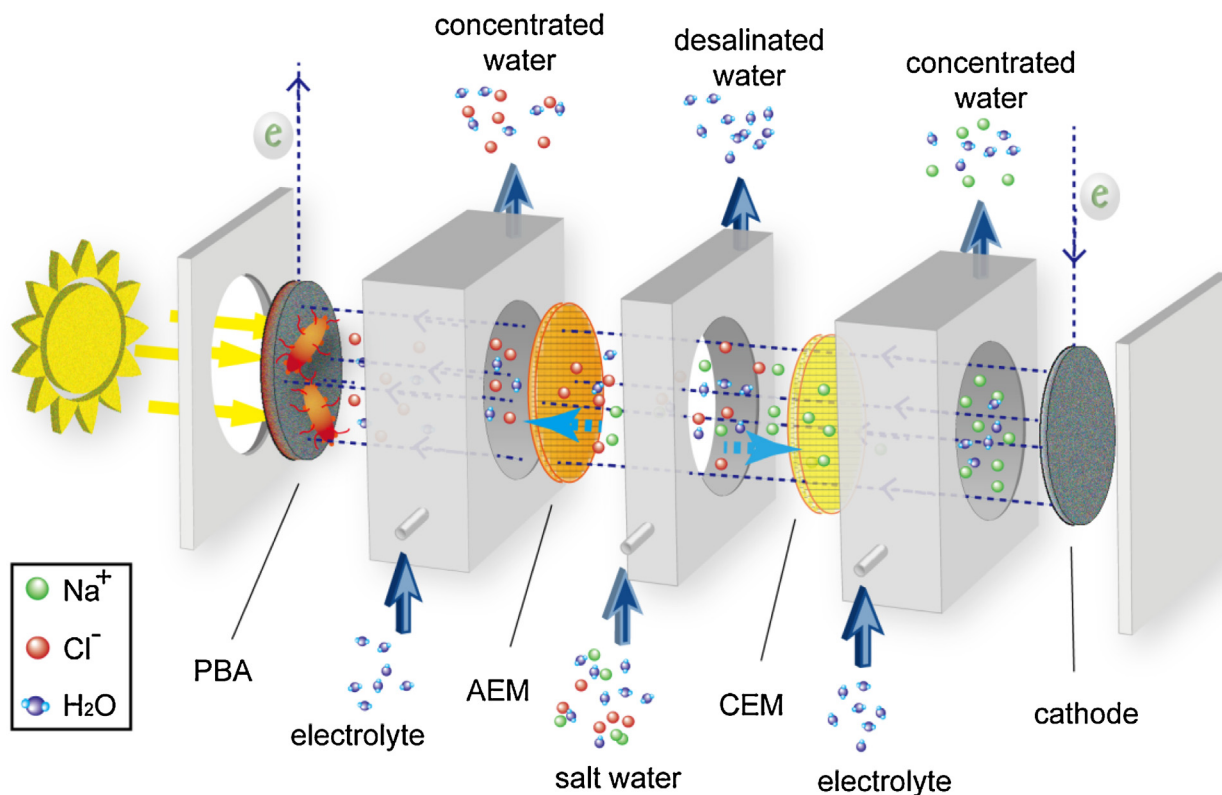
A circular graphite flake (diameter 40 mm, thickness 5 mm, projected surface area  $12.5\text{ cm}^2$ ) was used as the support for the nanostructured  $\alpha\text{-Fe}_2\text{O}_3$ . Before use, the flake was ultrasonically cleaned for 30 min using acetone, ethanol, and deionized (DI) water in turn. The  $\alpha\text{-Fe}_2\text{O}_3$  film anode was prepared by the anodization method as Fig. S1 [20]. First, the graphite flake was immersed into 0.5 M  $\text{FeSO}_4$  solution (ethylene glycol/ $\text{H}_2\text{O}$  = 1:8) and an anodization potential of 1.2 V vs Ag/AgCl was applied for 15 min using an electrochemical station (Biologic VSP, Claix, France). All potentials in this work are quoted relative to the Ag/AgCl reference electrode (3.5 M KCl). The obtained electrodes were sintered in a furnace at  $500\text{ }^\circ\text{C}$  for 2 h and then allowed to cool naturally to room temperature. Last, the unmodified side of the

anode was immersed in light liquid paraffin for 10 min (the photo-modified side did not touch the paraffin), and then cleaned to remove the excess paraffin using surfactant for 10 min.

### 2.2. Reactor construction and operation

The reactor was a sealed rectangular three-chamber (anode, middle desalination, and cathode) reactor (Fig. 1) which was separated with an anion exchange membrane (AMI-7001, Membranes International, USA) and cation exchange membranes (CMI-7000, Membranes International). The membranes were immersed in 5% NaCl solution for 24 h before use. The active volume of the anode, middle desalination, and cathode chamber were 40, 10, and 40 mL, respectively. Two reactors were constructed for the experiments: (a) PMDC: equipped with the PBA. The photo side of the PBA was pointed outwards to receive light from a xenon lamp (12V-35W, Shenlei, China), while the other side was pointed inwards for immobilization of the biofilm (projected surface area  $12.5\text{ cm}^2$ ); (b) MDC: equipped with an untreated anode in the same way as PMDC. The cathodes of both reactors were graphite felt (4 cm diameter and 0.4 cm thickness).

The anolyte consisted of  $\text{CH}_3\text{COONa}$  ( $1\text{ g L}^{-1}$ ), M9 solution [21] ( $\text{NH}_4\text{Cl}$ ,  $0.1\text{ g L}^{-1}$ ;  $\text{NaCl}$ ,  $0.5\text{ g L}^{-1}$ ;  $\text{KH}_2\text{PO}_4$ ,  $4.4\text{ g L}^{-1}$ ;  $\text{K}_2\text{HPO}_4$ ,  $3.4\text{ g L}^{-1}$ ;  $\text{MgSO}_4$ ,  $0.1\text{ g L}^{-1}$ ;  $\text{NaHCO}_3$ ,  $2\text{ g L}^{-1}$ ), and trace elements ( $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ,  $1.0\text{ mg L}^{-1}$ ;  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ,  $0.02\text{ mg L}^{-1}$ ;  $\text{H}_3\text{BO}_3$ ,  $0.014\text{ mg L}^{-1}$ ;  $\text{MnSO}_4\cdot 4\text{H}_2\text{O}$ ,  $0.10\text{ mg L}^{-1}$ ;  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ ,  $0.10\text{ mg L}^{-1}$ ;  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ ,  $0.02\text{ mg L}^{-1}$ ;  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ,  $0.02\text{ mg L}^{-1}$ ). The anolyte was flushed with high-purity nitrogen gas for 10 min before use. The catholyte was  $10\text{ g L}^{-1}$   $\text{K}_3[\text{Fe}(\text{CN})_6]$ . Both anolyte and catholyte were continuously recirculated through the anode and cathode chambers at a rate of  $2\text{ mL h}^{-1}$  using a peristaltic pump. The initial microorganisms for the reactor were collected from the



**Fig. 1.** Desalination mechanism of PMDC. First, the oxidation of organics by the microorganisms occurs spontaneously in the anode chamber. Second, the electrons are continuously attracted to the anode by the impetus from the electron holes and are then transferred to cathode. The bacterial extracellular electron transfer capacity is efficiency intensive. Finally, the water in the middle chamber is efficiently desalinated under the impetus of the inflow current.

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