Influence of Substrate Concentration on the Defluoridation Performance of Microbial Desalination Cell

Sravan J, Praveena Gangadharan, S. Shika

Abstract— Fluorides are introduced into the environment either naturally by fluoride bearing host rocks and volcanic ash, or by effluents from various industries like semiconductors, aluminium, etc. Drinking water with fluoride levels up to 1.5 mg/L is beneficial as it prevents dental decay, but concentrations > 1.5 mg/L cause dental and skeletal fluorosis. Existing efficient defluoridation techniques are energy-intensive, require chemical addition, and generate large amounts of sludge, which require further treatment prior to disposal. Recently, microbial desalination cells (MDCs) have been developed for desalination without the application of external energy. Microbial desalination cells are an emerging concept that uses bioelectric potential produced from microbial metabolism to carryout desalination. MDCs consist of three compartments the anode, the cathode, and a salt compartment, which is placed between the anode and the cathode. This study is a laboratory experiment to evaluate the effectiveness of using MDC technology to remove contaminated fluoride (F^-) ions in ground water. In this study we observe the cell efficiency according to the substrate concentrations of anode chamber. Here, we synthetically produce 3 mg/L concentration of fluoride solution which is to be placed in salt compartment (middle chamber). Substrate concentrations of 1.5 and 2 g/L acetate were placed on anode chamber along with sludge extracted from anaerobic reactor. Current generation and substrate degradation in anode chamber are also experimentally studying. The permissible level of 1.5 mg/L of F^- was achieved within 12 hrs for 2 g/L acetate concentration, while the 1.5 g/L acetate concentration took 18 hrs when, dimethyl sulfoxide (DMSO) coated carbon cloth (CC_{DMSO}) electrode was used in anode. Similarly, permissible limit obtained within 18 hrs for 2 g/L, while it takes about 24 hours to achieve permissible limit when bare carbon cloth (CC) were used. Also, maximum power density obtained in 2 g/L acetate concentration was 3.3-3.4 times higher than that of 1.5 g/L acetate concentration, both in CC_{DMSO} and bare CC.

Keywords — Acetate, Chemical oxygen demand, Defluoridation, Microbial desalination cell, Microbial fuel cell, Power generation, Substrate concentration.

1 Introduction

The Microbial Fuel Cell (MFC) is a bioelectrochemical system (BES) that can be used as a technology for wastewater treatment accompanied by energy recovery [5]. MFC has been widely considered as one of the promising method for sustainable energy production from organic wastes and biomass by using the catalytic activity of microorganisms to convert organic matters to energy production. In recent times, new renewable energy resources to replace fossil fuels are main focus. MFCs can be used as a substitute for the conventional activated sludge process [12]. Most of the existing technologies such as reverse osmosis, multi stage flash distillation, electro dialysis, membrane process etc demand high energy and cost [2], [10]. MDC is a three chambered BES which consists of an anion exchange membrane (AEM) next to the anode and a cation exchange membrane (CEM) by the cathode, and a middle chamber between the membranes filled with water that is being desalinated. Microbes located in anode compartment are used to degrade/convert organic and/or inorganic substrates through their metabolisms called Electro genesis [5]. MDC works on the basis of transfer of ions from water in the middle chamber in proportion to current generated by bacteria in the anode [7]. Groundwater is a vital source of water which supports human health, agriculture, and industrial development and plays a critical role in the sustainability and functioning of ecosystems. This paper concentrates on one such toxic element, fluoride. Fluorine, chlorine, and bromine are some of the halogen elements present in the drinking water and they are providing major issues in recent decades. Fluorine is considered an extremely required mineral by our human body but the excessive level of fluorine has affected more than 200 million people around the world [9]. Fluoride bearing minerals are the major cause of fluoride ions (F^-) in the groundwater. The alteration in the composition of the rocks due to fluoride ions, the minerals get dissociated, deposited, and weathered due to the variation in climatic factors. Hydroxyapatite is the main constituent found in teeth and bones. Fluorine helps in the prevention of tooth decay by displacing the hydroxide ions from hydroxyapatite. Thus, forming fluorapatite, this acts as a barrier and protects the teeth from acid attack. Further, excessive fluoride was ingested over a desired period, the teeth become denser and brittleness happens, this is termed as fluorosis. Fluorosis is

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considered as a public social health problem that can negatively affect the physical and mental health of patients and their families. Fluorosis is an incurable disease, so that suitable treatment techniques must be adopted for eliminating the excessive fluoride in contaminated water.

The performance of the MFC was found to be affected by the concentration of substrates [11]. When current is generated by bacteria on the anode, protons are released into solution and positively charged species are prevented from leaving the anode by the AEM and therefore negatively charged species move from the middle chamber to the anode. In the cathode chamber protons are consumed, resulting in positively charged species moving from the middle chamber to the cathode chamber [4]. The present study focuses on the performance of MDC under two different substrate concentrations in anode chamber. MDC performance was investigated in acetate concentrations of 1500 and 2000 mg/L until the fluoride concentration was reduced to the permissible limit of 1.5mg/L. Also we conducted experiments using dimethyl sulfoxide (DMSO) coated carbon cloth (CC_{DMSO}) as anode electrode.

2 METHODS AND MATERIALS

2.1 MDC setup

The MDC used in this study was a three-chamber bio electrochemical reactor made using plexiglass acrylic sheets (Fig. 1). The three chambers were separated with heterogeneous ion-exchange membranes: an anion-exchange membrane (Aqua treat) between the anode and middle chamber and cation exchange membrane (Aqua treat). Carbon cloth (3.2 x3.2 cm^2) was used as both anode and cathode electrode and were connected externally by a copper wire.

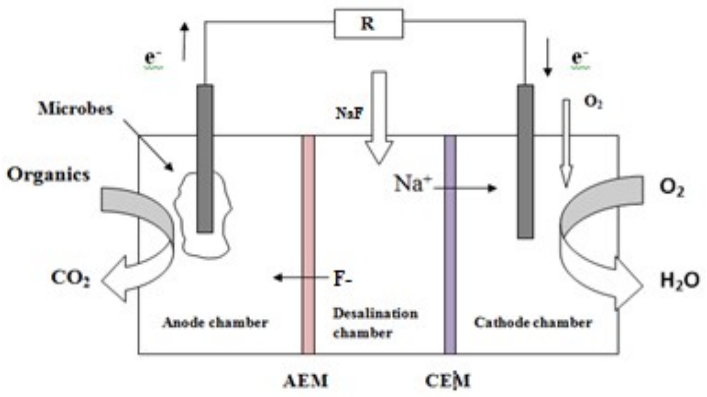

Fig. 1 Schematic diagram of a microbial desalination cell for water desalination showing anode, cathode and desalination chamber.

Both the anode and the cathode chamber held a liquid volume of approximately 100 mL each and the middle chamber contained a volume of approximately 75 mL. In a closed circuit, the external resistance was set at 1 Ω to achieve a high current generation. The Sodium (Na^+) ions moved into the cathode chamber through the cation-exchange membrane, and the Fluoride ions moved into the anode chamber through the anion-exchange membrane.

2.2 Operating conditions

A synthetic anode solution using acetate as carbon source was fed into the anode chamber (hydraulic retention time, HRT, of five days). The reactor was inoculated with anaerobic sludge obtained from an effluent treatment plant in Ahalya Medical College, Palakkad. The anode solution was prepared using (per L of Milli-Q water, 18.2 MΩ): sodium acetate 3 g; NaCl 0.5 g; $MgSO_4$ 0.015 g; $NaHCO_3$ 0.1 g; $CaCl_2$ 0.02 g; NH_4Cl 0.15 g; K_2HPO_4 1.07 g; KH_2PO_4 0.53 g; and trace elements, 1 ml [6]. Nitrogen gas was purged continuously to maintain anaerobic conditions in the anode chamber. Oxygen was used as a terminal electron acceptor in the cathode chamber. Phosphate buffer (10 mM) was used as the catholyte and was prepared using (per L of Milli-Q water) K_2HPO_4, 1.07 g/L; and KH_2PO_4, 0.53 g/L [1]. Synthetically prepared NaF solution of concentration 3 mg/L was added to the middle desalination chamber and monitored for fluoride reduction. Then, MDC performance was investigated in acetate concentrations of 1500 and 2000 mg/L until the fluoride concentration was reduced to the permissible limit of 1.5mg/L. Experiments were continued using dimethyl sulfoxide (DMSO) coated carbon cloth (CC_{DMSO}) as anode electrode.

2.3 Measurements and analysis

The cell voltage was recorded every 5 min by a data acquisition system (Keitheley DAQ). The pH and conductivity of the solutions were measured with a benchtop ion meter (HQ440D multi, Hach). Fluoride concentrations in all the three chambers were monitored by measurement using Ion selective electrode (Thermo scientific Orion star A214 pH/ISE Meter). The current (I) through the electrical circuit was determined from the measured voltage (E) according to $I = E/Re$, where Re is the external resistance. Wastewater treatment in terms of substrate degradation was determined by measuring the COD of the samples at regular intervals. The samples were centrifuged at 7,000 rpm for 10 minutes (Thermo scientific ST 8R centrifuge) and the supernatant was taken for COD analysis. The removal efficiency was calculated as given below,

$$Removal\ Efficiency\ (\%) = \left(\frac{A-B}{A}\right) * 100 \quad (1)$$

Where, A is the initial concentration and B is the observed concentration in mg/L.

3 RESULTS AND DISCUSSION

3.1 Defluoridation

Defluoridation efficiency of microbial desalination cell with bare carbon cloth and DMSO coated carbon cloth were shown in Fig 2(a) and Fig 2(b) respectively. There was an incremental pattern in defluoridation efficiency with the increase in concentration of acetate in anode chamber. Maximum Defluoridation efficiencies of 1.5 g/L and 2 g/L acetate were 49.15% and 60.99% respectively while using bare CC.

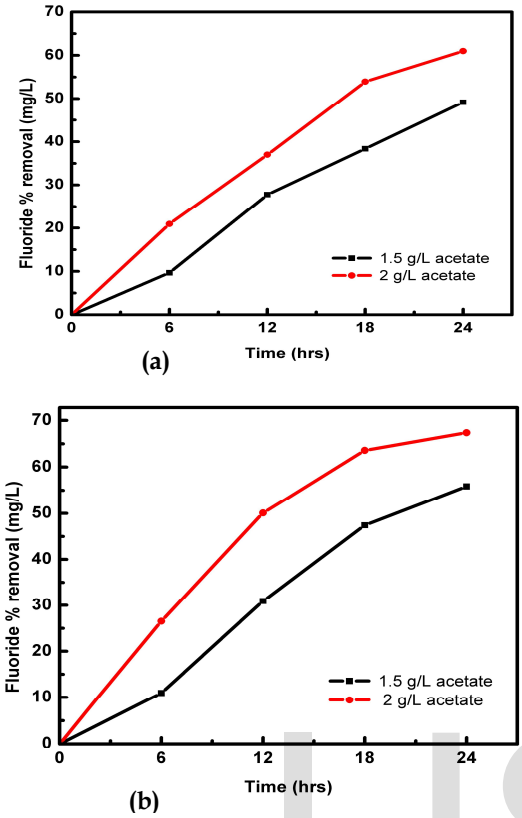

Fig. 2(a). Defluoridation efficiency of middle chamber as a function of time when using bare CC as electrode on 1.5 and 2 g/L acetate concentrations. **(b)** Defluoridation efficiency of middle chamber as a function of time when using CC_{DMSO} as electrode on 1.5 and 2 g/L acetate concentrations.

When we replace bare CC by CC_{DMSO} maximum defluoridation efficiency obtained were 55.85% and 67.37% for 1.5 g/L and 2 g/L acetate concentrations respectevely.

3.2 Substrate degradation

Substrate degradation in terms of COD removal in the anode chamber was monitored every 6 hr in 24 hr desalination cycle.

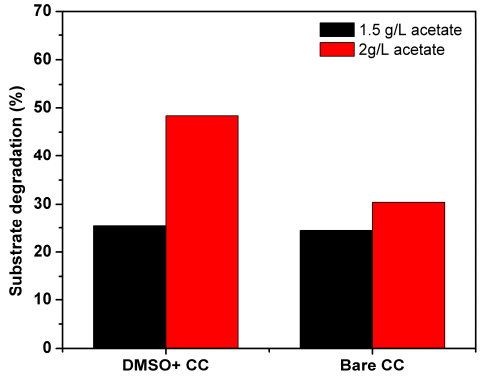

Fig. 3. COD removal in the anode chamber of MDC when different concentrations of acetate.

The bio-catalytic activity and substrate utilization play important role in developing the electrochemical gradient which determines the desalination in MDC [3].

When we use bare CC as electrode, 24.44% and 30.43 % were the substrate degradation efficiencies obtained respectively with 1.5 and 2 g/L acetate in the anode chamber. When we replace electrode by DMSO coated CC (CC_{DMSO}), substrate degradation obtained were 25.39% and 48.33% with 1.5 and 2 g/L respectively (Fig. 4).

3.3 Energy production

The polarization study conducted to characterize the performance of the MDC at different external resistances are shown in Fig. 4 (a) and (b) The external resistance was varied from 1 Ω to 10 M Ω after reaching a stable voltage production.

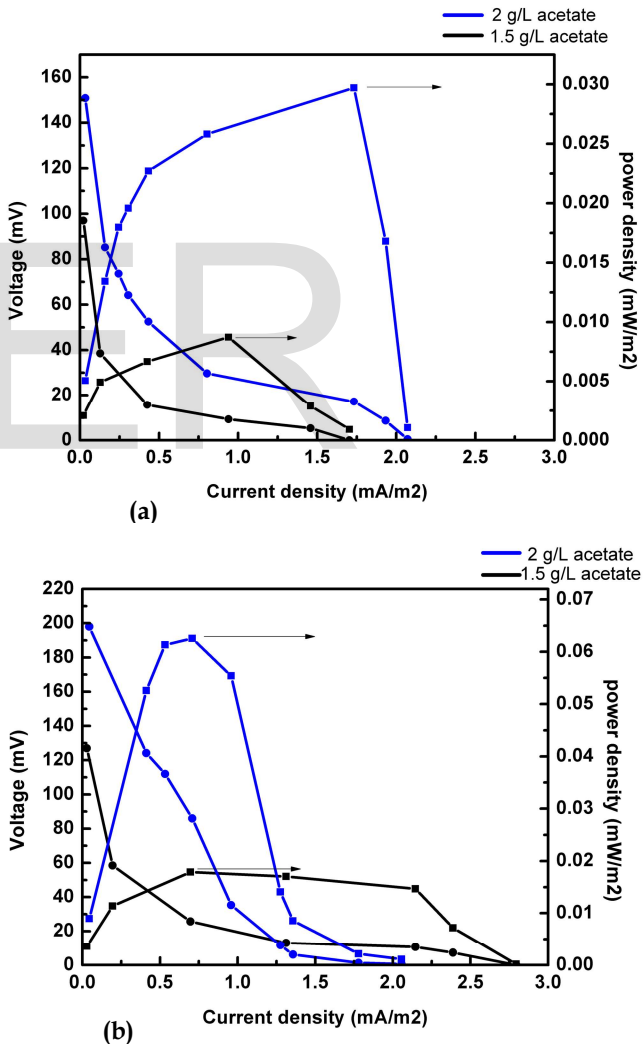

Fig. 4(a). Polarization profile showing the maximum power point on bare electrode. **(b)** Polarization profile showing the maximum power point on DMSO coated electrode.

Maximum power densities obtained in 2 g/L acetate concentration is about 29.37% higher than that of in 1.5 g/L

acetate concentration, where bare electrode in anode chamber. When we replace the bare electrode by CC_{DMSO} power density obtained in 2 g/L acetate concentration was about 28.02% higher than that of in 1.5 g/L acetate concentration.

4 Conclusion

The present study focused on the performance of MDC under two different substrate concentrations in anode chamber. Substrate used in this study was acetate at 1.5 and 2 g/L concentrations. Also, performance of MDC was observed at bare carbon cloth and DMSO coated carbon cloth (CC_{DMSO}). Performance of the MDC was found to be affected by the concentration of substrate. For a system fed with different concentrations of acetate solution, defluoridation efficiency and electricity production increased with COD concentration. Defluoridation efficiency obtained on different substrate concentration was in the range of 49- 67%. The defluoridation efficiency enhanced by replacing bare CC with DMSO coated CC as electrode in anode chamber. It is important to improve the existing MDC performance by optimizing MDC configuration, operation and electrode materials for higher desalination efficiency, extending this technology for the removal of numerous combinations of ions as well as for scaling up the system for field applications.

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References

[1] Brastad, K.S., He, Z., (2013). "Water softening using microbial desalination cell technology". *Desalination.* 851 https://doi.org/10.1016/j.desal.2012.09.

[2] Carmalin Sophia, A., Bhalambaal, V. M., Lima, E. C., and Thirunavoukkarasu, M. (2016). "Microbial desalination cell technology: Contribution to sustainable waste water treatment process, current status and future applications". *Journal of Environmental Chemical Engineering*, 4(3), 3468–3478.

[3] Hemalatha, M., Butti, S. K., Velvizhi, G., and Venkata Mohan, S. (2017) "Microbial mediated desalination for ground water softening with simultaneous power generation". *Bio-resource Technology*, 242, 28–35.

[4] Kim, Y. and Logan, B. E. (2011) "Series assembly of microbial desalination cells containing stacked electrodialysis cells for partial or complete seawater desalination". *Environmental Science and Technology*, 45(13), 5840–5845.

[5] Logan, B.E. (2008) "Microbial Fuel Cells". John Wiley & Sons, Inc., New York.

[6] Lovley, D. R. and Phillips, E. J. (1988) "Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese". *Applied and environmental microbiology*, 54(6), 1472–80.

[7] Mehanna, M., Saito, T., Yan, J., Hickner, M., Cao, X., Huang, X., and Logan, B. E. (2010)."Using microbial desalination cells to reduce water salinity prior to reverse osmosis". *Energy and Environmental Science*, 3(8), 1114–1120.

[8] Min, B. & Logan, B. E. (2004). "Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell". *Environmental Science and Technology*, 38(21), 5809–5814.

[9] S. Ayoob & A. K. Gupta (2006) "Fluoride in Drinking Water: A Review on the Status and Stress Effects", *Critical Reviews in Environmental Science and Technology*, 36:6, 433-487

[10] Saeed, H. M., Husseini, G. A., Yousef, S., Saif, J., Al-Asheh, S., Abu Fara, A., Azzam, S., Khawaga, R., and Aidan, A. (2015). "Microbial desalination cell technology: A review and a case study". *Desalination*, 359, 1–13.

[11] Ullah Z, Zeshan S. (2020)." Effect of substrate type and concentration on the performance of a double chamber microbial fuel cell". *Water Science and Technoogyl*;81(7):1336-1344

[12] Zhang, F., Ge, Z., Grimaud, J., Hurst, J. & He, Z. (2013). "Long-term performance of liter-scale microbial fuel cells treating primary effluent installed in a municipal wastewater treatment facility". *Environmental Science and Technology*, 47(9), 4941–4948.