



Wastewater Treatment in Pharmaceutical Company through Fuel Cell and Osmotic Membranes and Investigation of their Microbiological Effects

Mahya Bayat¹, Ahmad Riahi^{2,*}

¹Department of Water Treatment, Cinnagen Pharmaceutical Company, Karaj, Iran

²Department of Chemical Engineering, Faculty of Engineering, Payam Noor University, Tehran, Iran

Abstract Microbial fuel cell (MFC) and nano sized membrane bioreactor (NSMBR) are both promising technologies for wastewater treatment in pharmaceutical company, but both with limitations. In this study, a novel MFC–MBR integrated system, which combines the advantages of the individual systems, was proposed for simultaneous wastewater treatment and energy recovery. A new hybrid, air-bio cathode microbial fuel cell nano sized membrane bioreactor (MFC-MBR) system was developed to achieve simultaneous wastewater treatment and ultrafiltration to produce water for direct reclamation. The combined advantages of this system were achieved by using an electrically conductive ultrafiltration membrane as both the cathode and the membrane for wastewater filtration. In this study, an integrated MFC–MBR system was demonstrated to favor low-cost and efficient wastewater treatment and power generation. The nano sized membrane bioreactor (NSMBR) was used to guarantee the effluent quality and to provide a low-cost and effective bio-cathode for MFC, while the MFC promises an energy offset to the overall treatment process. An average current of 1.9 ± 0.4 mA was generated over a long period of about 40 days. The maximum power density reached 6.0 W m^{-3} . In addition, cost-effective materials were adopted for the system construction, suggesting a high economical attractiveness and practical applicability of this system. However, the nitrogen removal was limited due to the negative surface charge of the thin-film composite membrane and solution chemistry, which led to higher flux of ammonium toward the OMBR draw solution. This study reveals synergy between MFCs and OMBRs for sustainable wastewater treatment and energy production. This integrated system shows great promise for practical wastewater treatment application.

Keywords Microbial fuel cell (MFC), Nano sized membrane bioreactor (NSMBR), Bio-cathode, Microbial fuel cell, Osmotic nano sized membrane bioreactor

1. Introduction

Microbial fuel cells (MFCs) are devices that use bacteria as catalysts to oxidize various substrates and recover electricity. MFCs are promising for wastewater treatment processes pharmaceutical company, but to achieve practical application there are still many technical and cost obstacles to overcome. One approach to reduce the barriers and improve its applicability is to incorporate MFC into existing wastewater treatment processes. In this respect, a continuous-flow mode of operation is usually adopted, which is regarded as more suitable for practical wastewater treatment and MFC application [1]. Microbial fuel cells (MFCs) and osmotic nano sized membrane bioreactors (OMBRs) are two emerging technologies for sustainable wastewater treatment. While most studies focus on individual technology development, we hypothesize that these two processes can be mutually beneficial. MFCs use electrochemically active microorganisms to produce direct current from wastewater with less sludge production, but the current density is low from municipal wastewater due to its low conductivity and buffer capacity [1].



Another unknown factor is the FO membrane materials. Most existing OMBR and/or osmotic microbial fuel cell (OsMFC) studies were performed with cellulose triacetate (CTA) based FO membranes [2-3]. The non-porous FO membrane with lower fouling propensity acts as a barrier to the contaminants so provide a high-level wastewater treatment and reclamation. This work aims to investigate the feasibility of applying a relatively simple MFC–MBR integrated system for continuous wastewater treatment and power generation [1]. As one significant objective of this test was to investigate the feasibility to provide an efficient and cost-effective bio-cathode for MFCs by integrating MFCs with MBR, the volume of MFC anode chamber was designed smaller than that of MBR, so that the substrate availability at the anode and oxygen transfer at the cathode would be improved. Nevertheless, because of the great difference between the net volume of the anode and cathode chamber, the percentage of COD removed by the single MFC module was limited due to a short hydraulic retention time in the MFC. For practical application, more MFC could be submerged to the NSMBR system to increase the COD conversion to electricity. The NSMBR was used to guarantee the effluent quality and to provide a low-cost and effective bio-cathode for MFC, while the MFC promises an energy offset to the overall treatment process. In turn, the MFCs conditioned and reduced sludge production and therefore reduced forward osmosis (FO) membrane fouling. [4-5] the nitrogen removal was limited due to the negative surface charge of the thin-film composite membrane and solution chemistry, which led to higher flux of ammonium toward the OMBR draw solution. Further studies are needed to improve nitrogen removal, reduce fouling, and optimize system integration [6]. Osmotic nano sized membrane bioreactors (OMBRs) can be mutually beneficial when integrated together for wastewater treatment. Osmotic nano sized membrane bioreactors (OMBRs) are two emerging technologies for sustainable wastewater treatment. While most studies focus on individual technology development, we hypothesize that these two processes can be mutually beneficial [7,8].

2. Material and method

2.1 Nano-sized membrane bioreactor integrated system

2.1.1. Integrated MFC–MBR system

The diagram of the integrated MFC–MBR system. A non-woven fabric was used as the separator of the MFC part. Prior to use, the non-woven fabrics were first soaked in polytetrafluoroethylene solution, then dried to prevent water leakage. The anodic chamber was filled with self-fabricated activated carbon fiber [9]. The aeration tank, with a volume of 20 L, was used directly as the cathode chamber. The anode and cathode were connected through a 50 X resistor and the voltages were recorded automatically every 10 min using a data acquisition system (USB2801, ATD Co., China). For the NSMBR part, the nylon mesh with a pore size of 74 μm was used as the filter material. The membrane module with an effective filtration area of 1000 cm^2 was submerged into the aeration tank. Aeration units were placed at the bottom of the module. In order to suit the incorporation of MFC into MBR, the MBR's influent line was slightly altered. The MFC was inserted with two silicone tubes on the top and bottom of anodic chamber. Synthetic wastewater was continuously pumped into the MFC module through the bottom silicone tube using a peristaltic pump (Lange Co., China). The preliminarily treated wastewater in MFC module then flew into the aeration tank of the NSMBR for further treatment [10,18].

2.2. Inoculation and operation of the system

Some of mL mixture of anaerobic and activated sludge collected from laboratory bioreactors was injected as inoculum into the anodic zone from the bottom tube of the MFC. In order to enrich the electroactive bacteria for both anode and cathode, the MFC module was initially submerged in an activated sludge reactor and operated at a continuous-flow mode. The flow rate was much lower than that selected for the coupled system. In the wastewater 50 mL phosphorus buffer was added. But with the accumulation of anodic biomass, the microorganisms in effluent of MFC decreased significantly. The enrichment process lasted for about 30 days. After reaching a stable status for about 1 week, the MFC module was transferred to the aeration tank of the NSMBR and the coupled system began to work after small modification of MBR's influent pipe. The chemical oxygen demand (COD) concentration of the synthetic wastewater was 400 mg L^{-1} which was close to the concentration of domestic wastewater. The COD concentrations of the effluents from the MFC and the integrated system were measured according to the Standard Method [19,20]. Prior to measurements, all samples were filtered through a 0.45 μm membrane filter.



3. Result and Discussion

3.1. Morphological and electrochemical analysis

The biofilm attached on the cathode was characterized by scanning electron microscopy (SEM) [20]. To characterize the potential of catalyzing the oxygen reduction by the cathodic biofilm, cyclic voltammetry (CV) of the biofilm was performed using an electrochemical workstation with a three-electrode system. The reactor influent was used as the electrolyte. To identify the position of oxygen reduction peak, CV of the biofilm was repeated in the original electrolyte bubbled with nitrogen and air respectively. The polarization curves of MFC were obtained by varying the circuit external resistance from 10 to 10,000 Ω when the cell voltage of the MFC was relatively stable. Coulombic efficiency (CE) of MFC was calculated as $CE = C_p/C_{th}100\%$, where C_p is the total coulombs calculated by integrating the current over time, and C_{th} is the theoretical amount of coulombs available based on the COD removed in the MFC.

The NSMBR was used to guarantee the effluent quality and to provide a low-cost and effective bio-cathode for MFC, while the MFC promises an energy offset to the overall treatment process. An average current of 1.9 ± 0.4 mA was generated over a long period of about 40 days. Fig1. (a) Current generation of the system in over 40-day operation, (b) polarization and power density curves for the MFC. Fig. 2. (a) Effluent COD concentration; (b) COD removal efficiency of the integrated system; (c) MLSS concentration in the MBR. Fig. 3. Microstructure and electrochemical properties of the bio-cathode. (a) SEM images of graphite felt; (b and c): SEM images of biofilm on graphite felt; (d): Cyclic voltammogram of the microorganisms on the cathode in r substrate at a COD of 400 mg L⁻¹; s substrate then bubbled with nitrogen for 10 min; t substrate bubbled with air for 10 min; and u cyclic voltammogram of fresh graphite felt in the substrate. The substrate had the same composition as the influent of the integrated system. The maximum power density reached 6.0 Wm⁻³. Nevertheless, further improvements in system design and operating conditions are still needed to enable a better wastewater treatment performance and higher power generation.

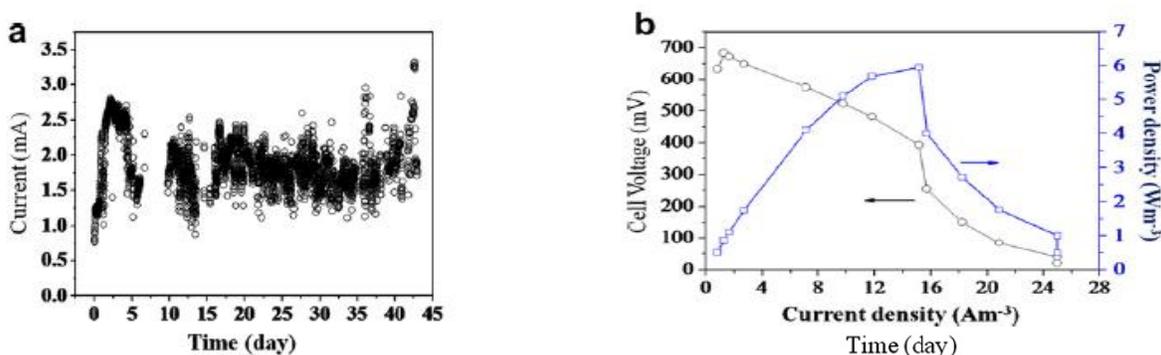


Figure 1: (a) Current generation of the system in over 40-day operation, (b) polarization and power density curves for the MFC

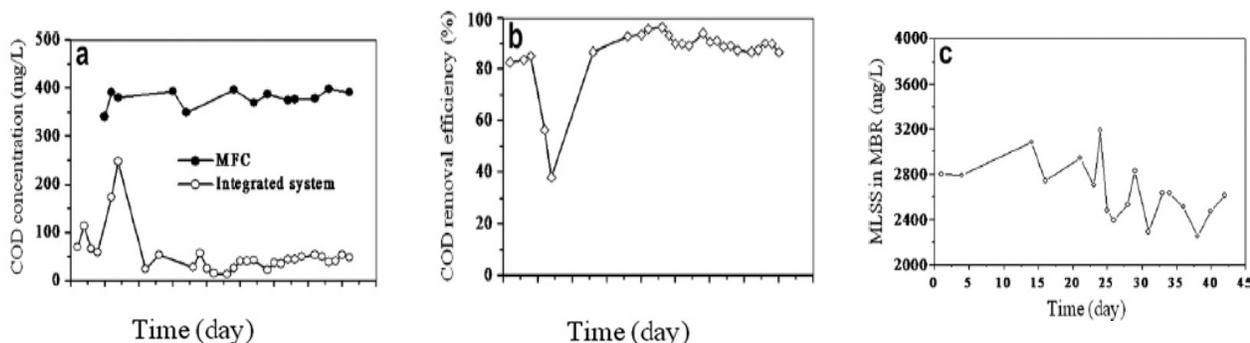


Figure 2: (a) Effluent COD concentration; (b) COD removal efficiency of the integrated system; (c) MLSS concentration in the MBR



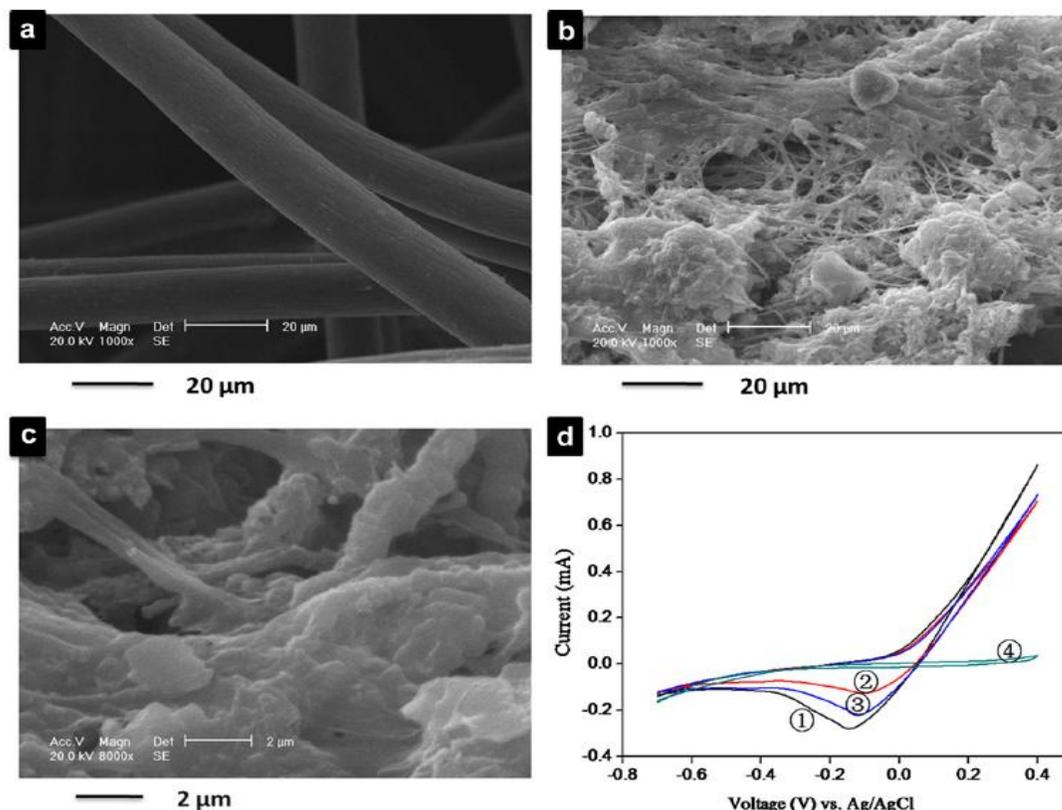


Figure 3: Microstructure and electrochemical properties of the bio-cathode. (a) SEM images of graphite felt; (b and c): SEM images of biofilm on graphite felt; (d): Cyclic voltammogram of the microorganisms on the cathode in *r* substrate at a COD of 400 mg L⁻¹; *s* substrate then bubbled with nitrogen for 10 min; *t* substrate bubbled with air for 10 min; and *u* cyclic voltammogram of fresh graphite felt in the substrate. The substrate had the same composition as the influent of the integrated system

3.2 Osmotic Nano Sized Membrane Bioreactors Have Mutual Benefits

3.2.1 Membranes and chemicals

A commercial TFC FO membrane (Hydration Technology Innovations, Albany, OR) was used in this study. The membrane has a water permeability NaCl permeability, and a structure parameter. Membrane coupons were soaked in MilliQ water at room temperature for over 24 h before use. Glucose-based defined medium was used as the synthetic feed wastewater, so degradation and mass transfer mechanisms can be understood [2,15].

3.2.2 Reactor configuration and operation

The schematic diagram of the two-stage MFC-OMBR system. The system consists of two parallel MFCs and one OMBR, which are hydraulically connected in series. The MFCs were inoculated with the anaerobic digested sludge collected from Boulder Wastewater Treatment Plant and fed with the synthetic wastewater. In the OMBR, a tubular membrane module with active layer facing feed orientation was fully submerged into a bioreactor. A magnetic stirrer bar was used to mix the solution in the OMBR at a speed of 400 rpm. In Run 1, fresh medium was used after system inoculation, and no membrane cleaning was performed during the run. In Run 2, the same operation was performed, but the membrane was chemically cleaned each day to investigate the difference in membrane fouling behavior. The chemical cleaning procedure included 30 min alkaline wash followed by 30 min acid wash. In Run 3, similar operation was used as Run 1, except 2000 mg total suspended solids (TSS)/L anaerobic sludge was added together with the medium into the MFC-OMBR system to understand if MFCs could serve as a pre-treatment to



reduce membrane fouling. The flow was controlled by the volume of permeate extracted from the OMBR. When the water level of the OMBR dropped below the designated value, fresh feed wastewater converged with the same amount of bulk solution from the OMBR was firstly transferred into the two MFCs in parallel then into the OMBR using a peristaltic pump. Conductivity, temperature, pH, oxidation-reduction potential (ORP) values in the OMBR were monitored and logged using Lab- VIEW. In the meanwhile, draw solution was recirculated at a cross flow velocity. The concentration of DS was monitored by conductivity measurements and maintained constant through dosing a stock solution. The water flux was determined gravimetrically by weighing the mass of permeate water collected at predetermined time intervals with a digital balance [4,9].

3.3 Analyses

All samples for sCOD, N and P measurements were filtered through 0.45 mm cellulose membranes (Millipore), and the sludge was used for TSS measurements. sCOD and TSS were measured according to standard methods described in detail by American Public Health Association. NH₃eN and PO₄eP were measured with HACH test tubes. All samples were collected and analyzed in triplicate. It should be noted that the samples collected from the MFC-OMBR system were replaced by the same amount of fresh wastewater. The voltage across an external resistor (R, 10 Ω) over the MFCs was recorded every 10 min using a data acquisition system. [2,6]

The MFCOMBR system effectively removed organics and phosphorus at mesophilic condition, producing a high quality effluent, accompanied with increased power production (up to 11.5 W/m³) and less membrane fouling. Fig. 4. Maximum power production from the MFCs during Run 1 and Run 2. Run 1: no sludge dose and without daily membrane cleaning; Run 2: no sludge dose and with daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments. Fig. 5. Time-course changes of sCOD concentrations in the MFC effluent, OMBR bulk solution, and draw solution, as well as the COD removal during Run 1. Run 1: no sludge dose without daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments. Fig. 6. Time-course changes of (a) NH₃eN and (b) PO₄eP concentrations in the OMBR bulk and draw solution during Run 1 and Run 2. Run 1: no sludge dose and without daily membrane cleaning; Run 2: no sludge dose and with daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments. The pre-treatment from MFCs reduced membrane fouling for the OMBR, credit to low sludge production (0.076 ± 0.008 gTSS/ gCOD), low sludge load (<350 mg/L TSS), and conditioned sludge property. While the study demonstrates the feasibility and potential, more research is needed to improve nitrogen removal, reduce fouling, and optimize system integration.

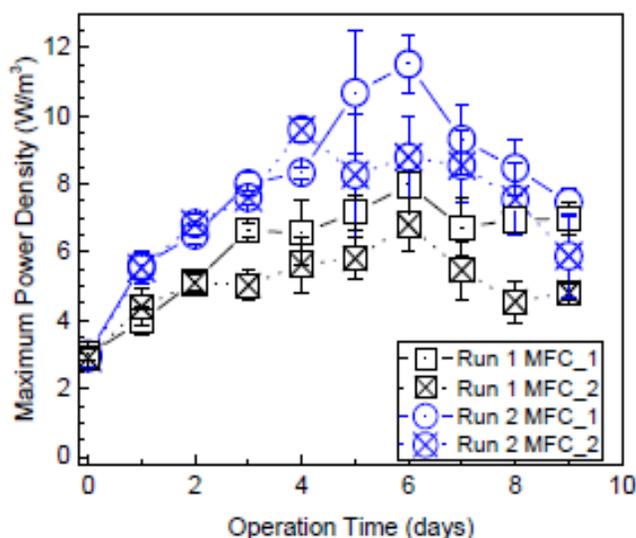


Figure 4: Maximum power production from the MFCs during Run 1 and Run 2. Run 1: no sludge dose and without daily membrane cleaning; Run 2: no sludge dose and with daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments.



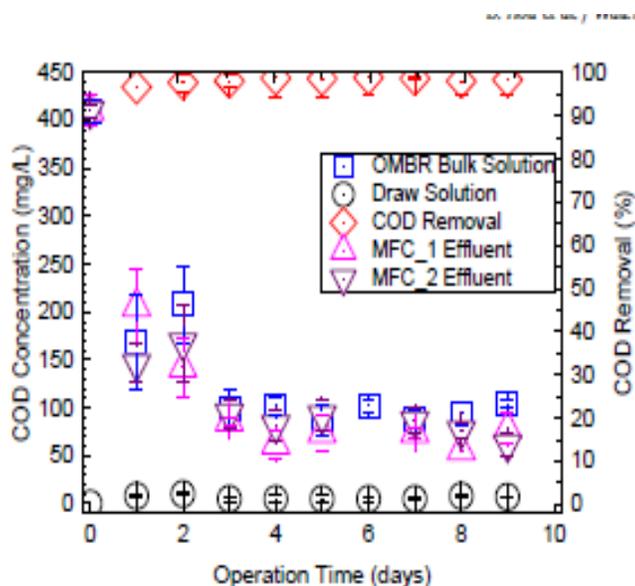


Figure 5: Time-course changes of sCOD concentrations in the MFC effluent, OMBR bulk solution, and draw solution, as well as the COD removal during Run 1. Run 1: no sludge dose without daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments.

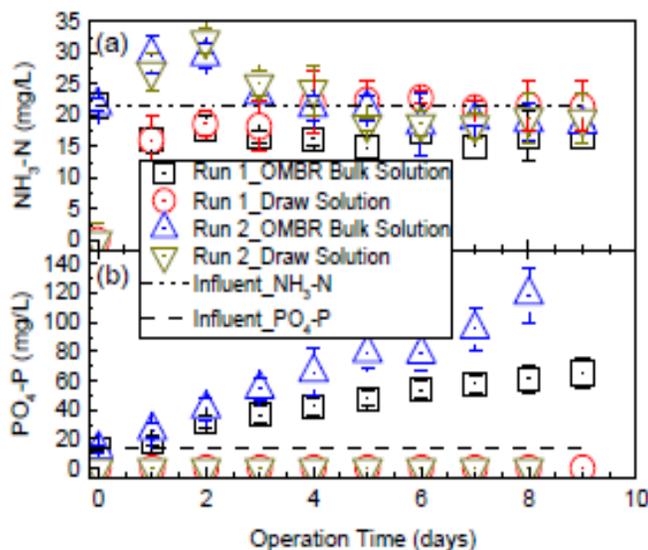


Figure 6: Time-course changes of (a) $\text{NH}_3\text{-N}$ and (b) $\text{PO}_4\text{-P}$ concentrations in the OMBR bulk and draw solution during Run 1 and Run 2. Run 1: no sludge dose and without daily membrane cleaning; Run 2: no sludge dose and with daily membrane cleaning. The error bars represent the standard deviations based on three independent experiments.

4. Conclusion

In this study, an integrated MFC–MBR system was demonstrated to favor low-cost and efficient wastewater treatment and power generation. The NSMBR was used to guarantee the effluent quality and to provide a low-cost and effective bio-cathode for MFC, while the MFC promises an energy offset to the overall treatment process. The MFCOMBR system effectively removed organics and hosphorus at mesophilic condition, producing a high quality effluent, accompanied with increased power production (up to 11.5 W/m³) and less membrane fouling. The MFCs were benefited from the accumulation of buffer capacity and solution conductivity by the OMBR, leading to reduced

internal resistance and increased power generation. Never the less, further improvements in system design and operating conditions are still needed to enable a better wastewater treatment performance and higher power generation.

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References

- [1]. Wang, Y. P., Liu, X. W., Li, W. W., Li, F., Wang, Y. K., Sheng, G. P., Zeng, R.J. & Yu, H. Q. (2012). A microbial fuel cell–membrane bioreactor integrated system for cost-effective wastewater treatment. *Applied Energy*, 98, 230-235.
- [2]. Hou, D., Lu, L., & Ren, Z. J. (2016). Microbial fuel cells and osmotic membrane bioreactors have mutual benefits for wastewater treatment and energy production. *Water research*, 98, 183-189.
- [3]. Chang, W. K., Hu, A. Y. J., Horng, R. Y., & Tzou, W. Y. (2007). Membrane bioreactor with nonwoven fabrics as solid–liquid separation media for wastewater treatment. *Desalination*, 202(1-3), 122-128.
- [4]. Fan, B., & Huang, X. (2002). Characteristics of a self-forming dynamic membrane coupled with a bioreactor for municipal wastewater treatment. *Environmental science & technology*, 36(23), 5245-5251.
- [5]. Fuchs, W., Resch, C., Kernstock, M., Mayer, M., Schoeberl, P., & Braun, R. (2005). Influence of operational conditions on the performance of a mesh filter activated sludge process. *Water research*, 39(5), 803-810.
- [6]. Kiso, Y., Jung, Y. J., Ichinari, T., Park, M., Kitao, T., Nishimura, K., & Min, K. S. (2000). Wastewater treatment performance of a filtration bio-reactor equipped with a mesh as a filter material. *Water Research*, 34(17), 4143-4150.
- [7]. Ren, X., Shon, H. K., Jang, N., Lee, Y. G., Bae, M., Lee, J., Cho, K. & Kim, I. S. (2010). Novel membrane bioreactor (MBR) coupled with a nonwoven fabric filter for household wastewater treatment. *Water research*, 44(3), 751-760.
- [8]. Aaron, D., Tsouris, C., Hamilton, C. Y., & Borole, A. P. (2010). Assessment of the effects of flow rate and ionic strength on the performance of an air-cathode microbial fuel cell using electrochemical impedance spectroscopy. *Energies*, 3(4), 592-606.
- [9]. Achilli, A., Cath, T. Y., Marchand, E. A., Childress, A. E., (2009). The forward osmosis nano sized membrane bioreactor: a low fouling alternative to NSMBR processes. *Desalination* 239 (1e3), 10e21.
- [10]. APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 20th Ed. APHA American Public Health Association. Brown, R. K., Harnisch, F., Dockhorn, T., Schröder, U., 2015.
- [11]. Examining sludge production in bioelectrochemical systems treating domestic wastewater. *Bioresour. Technol.* 198, 913e917.

