Effect of batch vs. continuous mode of operation on microbial desalination cell performance treating municipal wastewater

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Article Information

Abstract

Microbial desalination cells (MDCs) have great potential as a cost-effective and green technology for simultaneous water desalination, organic matter removal and energy production. The aim of this study was to compare the performance of a MDC under batch and continuous feeding conditions. Hence, power and current output, coulombic efficiency, electron harvest rate, desalination rate and COD removal were calculated during the operation. According to the obtained results, the MDC performance exhibited some changes when the reactor switched from batch to continuous mode. The continuously operated MDC indicated a maximum power density of 15.9 W.m⁻³ and an average salt removal rate of 80%. In comparison, the batch MDC demonstrated the maximum power density and average salt removal rate of 13.9 W.m⁻³ and 68.1%, respectively. In addition, 83.7% of COD was removed in the continuously fed MDC at a hydraulic retention time of two days, which was 13.8% more than amount of COD removed in MDC under a two days batch process. The obtained results revealed that enrichment of anolyte under controlled continuous feeding conditions would relatively improve the MDC performance.

1. Introduction

Pure water is an essential necessity in every aspect of human life. Scarcity of water has become a critical issue due to the high rate of population growth, inadequacy of water supply and water resources pollution. Complicated, expensive and energy-intensive water purification technologies will reduced clean water resources by one-third in the near future [1]. Therefore, seawater and brackish water desalination has received great attention in recent years [2]. The main problem of the conventional desalination processes, such as thermal distillation and membrane processes, are their high energy
consumption [3].

The microbial fuel cell (MFC) is an efficient technology which produces a new alternative energy source from wastewater. A MFC has several advantages over other types of energy generators such as zero pollution and higher efficiency [4]. In recent years, new fuel cells have been developed which use bacteria to create renewable energy in the form of electricity, hydrogen and methane. Although bioelectricity production via bacteria was first observed by Potter et al. in 1911 [5], more useful functions were developed during the next 50 years [6-9]. Finally, in the early 1990s, MFC became known as a promising technology to achieve energy and treat wastewater [6].

A microbial desalination cell (MDC) is a modified form of a conventional bio-electrochemical process which shares similar features with microbial fuel cell. MDC can be simultaneously be used for salt removal, wastewater treatment and energy production [10]. MDC also requires lower energy compared to other desalination process such as reverse-osmosis or electro-dialysis [11]. In the anode chamber of a MDC, active exo-electrogenic bacteria degrades organic matters and release electrons. At the cathode compartment, hydrogen is consumed by electrons through reduction reaction of electrons acceptors [12]. Consequently, in order to achieve a charge balance, salt ions migrate from the middle chamber into the anode and cathode chamber allowing water to be successfully desalinated [13]. Cao et al. [14] introduced the first conventional three chamber MDC and extended works have been reported afterwards. In recent years, MDC performance has been improved by various design configurations, electrode materials and electrolytes under batch and continuous operation [9,13]. The latest emerging MDCs have several advantages such as having low cost, high efficiency and low energy requirements [15]. According to recent work, MDC can be operated under different operational mode including; batch [11,14], fed-batch [8,16] and continuous [17,18]. In the latest reported literature on batch MDCs [19,20] nitrogen, heavy metal and ammonia removals were investigated. MDCs have also exhibited high efficiency in treatment of synthetic copper-containing wastewater [21]. Jacobson et al. [17] indicated that an up-flow continuously fed MDC can produce a maximum power density of 30.8 W.m$^{-3}$ when synthetic wastewater was used. Lay et al. [22] compared power generation in a MFC using synthetic wastewater under continuous and fed-batch operation. In the MFC operated in a fed-batch condition, a maximum power density of 356 mW.m$^{-2}$ was reported. While, a maximum power density of 372 mW.m$^{-2}$ was found in the continuously fed MFC as reported in [22]. Pannell et al. [23] have investigated treatment of wastewater under fed-batch vs. continuous operation. Based on the reported data, the current density obtained in the continuously fed MFC was about two times more than the fed-batch MFC [23]. Although some investigations have compared the effect of operational conditions on MFC performance; there is no comparative study on the operational mode in MDC so far. In addition, there are only a few studies which have employ MDC technology for treating municipal wastewater and evaluated the effect of operation mode on reactor performance. The present work investigated the bioelectricity production, biodegradation of organic matters and salt removal in a three-chamber MDC under batch and continuous conditions. Municipal wastewater was used as substrate in both anode and cathode compartments.

2. Materials and methods

2.1. MDC construction

The MDC was constructed by connecting three cubic Plexiglas chambers, an anode and cathode chamber with equal dimensions (10 × 10 × 2.5 cm), and a desalination chamber (10 × 10 × 0.3 cm) inserted in middle of the MDC reactor. The anode and desalination chamber were physically separated by an anion exchange membrane (AEM, Mega, Czech
Republic). Cathode and desalination chamber were also separated by a cation exchange membrane (CEM, Mega, Czech Republic). Total volume of anode, desalination and cathode chamber after inserting electrodes and air-diffuser were 200, 30 and 180 mL, respectively. Carbon cloths (without Pt catalyst) were used as the anode and cathode electrode. In order to remove trace elements, electrodes were washed for 48 h in 1 M HCl and rinsed with deionized water before use. The electrodes were connected to an external resistance through a copper wire under a fix resistance of 100 Ω in a closed circuit condition. No resistance was employed in the open circuit condition. A schematic diagram and actual image of the continuous MDC set up is depicted in Fig. 1.

2.2. MDC operation

The anode chamber of the MDC was inoculated by a previously enriched exo-electrogenic consortium of an old MDC (50%, v/v) to accelerate power generation and bacterial adhesion on the electrodes. Actual domestic wastewater obtained from a local municipal wastewater treatment plant (Babol, Iran) was used as both anolyte and catholyte solutions. The untreated wastewater used in this study had an average chemical oxygen demand (COD) of 615 ± 30 mg.L⁻¹, conductivity of 7.12 ± 0.49 mS.cm⁻¹, pH value of 6.98 ± 0.085, total suspended solid (TSS) of 192 mg.L⁻¹, biological oxygen demand (BOD) of 304 ± 12 mg.L⁻¹, total nitrogen (TN) of 36 mg.L⁻¹ and total organic carbon (TOC) of 141 mg.L⁻¹. Before operation, the anode chamber was deoxygenated with nitrogen gas. The same solution as the anode chamber was used in the cathode compartment. The cathode solution was aerated at a constant flow-rate in order to supply a dissolved oxygen level of 4 mg.L⁻¹. The salt solution in the middle compartment had an initial NaCl concentration of 35 g.L⁻¹. All experiments were conducted at a room temperature of 22 ± 2 °C. After establishment of biofilm on the anode electrodes, the MDC was evaluated under batch condition. In the batch experiments, solutions in all chambers were replaced after two days. In a second series of experiments, the MDC was operated under continuously fed operation with a flow rate of 0.07 mL.min⁻¹, giving an hydraulic retention time (HRT) of two days. The salt solution in the middle chamber was replaced every two days in all experiments. All samples were analyzed in triplicate and the average

![Fig. 1. A) Schematic diagram of MDC set up in the lab, B) actual image of MDC set up.](image-url)
values were reported.

2.3. Measurement and calculations

The produced voltage (V) across the external resistor (R_e) in the MDC was measured every 20 min using a multimeter with a data acquisition system (AEP, DG40, Iran). Obtained voltage was converted to current (I) and power (P) according to I = V/R_e and P = V×I, respectively. Conductivities and pH of solutions were measured using a conductivity meter (EC215, Hana, Italy) and pH meter (pH211, Hana, Italy), respectively. The concentration of COD was calculated according to procedures outlined in the standard method using a spectrophotometer (UNICO 2100, USA) [24]. The polarization curve was determined according to Watson et al. [25]. The coulombic efficiency (CE) was measured as the total coulombs (C) transferred to the anode chamber from the substrate to the maximum possible amount of coulombs obtainable from the removed substrate. Columbic recovery (CR), which describes conversion efficiency, was determined using total amount of substrate fed into the anode chamber, instead of substrate removed in the anode. CE (%), CR (%) and energy harvest rate (C.h⁻¹) are calculated by Eqs. (1), (2) and (3):

\[
CE = \left[ \frac{M \sum_{i=1}^{n} I_{t_i}}{FbC_i V} \right] \times 100\%
\]

\[
CR = \left[ \frac{M \sum_{i=1}^{n} I_{t_i}}{FbC_{total} V} \right] \times 100\%
\]

\[
I_{t_i} = \frac{\sum_{i=1}^{n} I_{t_i}}{\sum_{i=1}^{n} t_i}
\]

where I_i (A) is the produced current during time t_i (s) is the interval time over which data are collected, F is Faraday’s constant (96485 C per mole of electron), b is the mole of electron per mole of substrate, C_r is COD removal within time t (g.L⁻¹), C_total is the initial COD concentration of substrate in anode chamber, V is the anolyte volume (L) and M is the molecular weight of oxygen (32 g.mol⁻¹).

3. Results and discussion

3.1. Start up and current production of MDC

In the current study, a MDC was operated under two different modes: continuous and batch mode, feeding with actual municipal wastewater. The electrical energy produced by the MDC was determined by measuring voltage across a fixed external resistor of 100 Ω during the operation. The current was calculated by the ohm’s low method in order to produce an appropriate biofilm on the electrodes. In addition, the anolyte of an old matured MDC was inoculated to the MDC reactor to produce a quick start up. During start up, the electrical current rose, and the conductivity of the salt solution had a maximum removal of 32%. After approximately 10 days, a steady state condition was observed in both MDCs. The maximum open circuit voltage up to 960 and 920 mV was produced in continuous and batch mode, respectively. The corresponding voltage values decreased to 684 mV and 636 mV when the MDCs were operated under a fix external resistance of 100 Ω. These results are higher than three-chamber MDC previously reported using actual municipal wastewater [26]. Fig. 2 demonstrates the current variation in the continuously-fed MDC compared to the batch MDC over the whole duration of the experiments. The purpose of this comparison was to determine the current production efficiency with time in two set of experiments. According to obtained data, at HRT of two days, the current trend rose from 0.2 to 6 mA during the initial 7 days and then remained relatively constant during the rest of the experiment. While in the batch MDC, the produced current increased dramatically to 6 mA followed by a gradual decrease to 4.2 mA over every single batch cycle due to the reduction of salt
concentration and increasing internal resistance of the reactor. This decline can be attributed to the consumption of substrate by bacteria in the anolyte chamber as well. Fluctuations seen in current trend were due to the inactivity of some types of microbes which compete with electrochemically active bacteria to consume available substrate. The anolyte pH in both the batch and continuously fed MDC dropped from 6.98 ± 0.085 to 5.23 ± 0.068 and 5.98 ± 0.081, respectively. This decline was attributed to anaerobic activity of microorganisms and proton accumulation. The catholyte pH increased from 6.98 ± 0.085 to 8.62 ± 0.087 and 8.04 ± 0.096 in the batch and continuously operated MDC, respectively, mainly due to consumption of protons in the cathode chamber. The pH variation in the anode and cathode chamber was similar to previously reported MDCs using actual wastewater and bio-catholyte under batch condition [26].

Fig. 2. Variation of generated current by time in MDCs under batch and continuous condition using an initial salt concentration of 35g/l and external resistance 100 Ω.

3.2. Polarization and power density curves

During operation energy was continuously generated. Polarization and power density curves were plotted by decreasing the external resistances from 10 kΩ to 1 Ω stepwise in 20 min intervals using a resistance box. The polarization curve shows voltage (as a function of current), electricity production and internal resistance of MDC. The internal resistance of the MDC was determined by the measured polarization slope [27]. Maximum power is obtained when the internal and external resistance of system are equal [28]. The plots indicated that the power density of the MDC is a function of periodic increase in the external resistance. As it is indicated in Fig. 3, the polarization curve showed the maximum power density of 15.9 and 13.93 W.m⁻³ under continuous and batch condition, respectively (based on an anode chamber volume of 200 mL). In addition, the power produced in this study was higher than previous research conducted with the same three-chamber MDC which achieved a 3.6 W.m⁻³ power density during 50 day operations using actual domestic wastewater as anolyte and a ferricyanide phosphate buffer solution as catholyte [29]. Comparison results by data reported in different literature reveals that different maximum power density may be achieved by similar three-chamber MDCs due to differences of electrochemical activity of bacteria [26]. Internal energy losses were the important component which determine the scale of power output [6]. Produced voltages led to an internal resistance of 156 and 147 Ω in the batch and continuously fed MDC, respectively. The slightly higher internal resistance in continuous operation was likely because of mass transfer improvement close to the electrodes as well as increasing ion transfer efficiency to the membranes.

Fig. 3. Polarization curve; power density (open symbols) and voltage (filled symbols) of the MDCs under batch and continuous condition.
MDCs have several products including electricity production and water desalination. In order to obtain the highest energy generation, a MDC should be operated at their maximum power output, in which external resistance is equal to internal resistance. When desalination efficiency is more important than power generation, a MDC should be run at the highest current which leads to high desalination productivity. In this study the first condition (highest power production) was used. When a MDC works as a pre-desalination process energy produced during operation can be used by downstream desalination processes. Therefore, a counterbalance will exist between high power output and low desalination efficiency.

3.3. COD removal and columbic efficiency

Fig. 4 demonstrates the influent and effluent COD concentration (mg.L\(^{-1}\)) and COD removal efficiency (%) in the anode chamber of the MDCs under batch and continuous mode during operation. Constant COD removal and output voltage was an indicator of stable performance of the MDC under the given condition. As it is indicated in both experiments, the batch MDC as well as the continuously operated MDC indicated an effective COD removal (approximately up to 70%) while the COD concentration decreased during the time. Maximum COD concentrations in the anode chamber dropped from 610 to 99 and 175 mg.L\(^{-1}\) under continuous and batch condition, respectively. The main reason for this drop can be attributed to anaerobic digestion of organic matter in the anode chamber. Feeding the anolyte chamber at HRT of two days led to an average COD removal of 83.7%. COD removal in the batch MDC gradually increased to an average amount of 37.7 and 69.9% during the first and second day of operation over every single batch cycle. These results show that the COD removal in continuous operation improved compared to COD removal efficiency in every single batch process, probably because of the different substrate available in the two reactors (batch and continuous). Greater COD removal efficiency under continuous condition was also due to the fact that continuous flow operation prevents large pH variation in the anode and cathode chamber compared to the batch process.

Columbic efficiency demonstrates the amount of electrons which are obtainable from the substrate for producing the electrical current. It is defined as the ratio of the actual amount of electrons gained by the substrate to the theoretical amount of electrons obtained by the bacteria based on COD removal as outlined in the material and method section. The CE changes could not be determined correctly in the first 10 days of operation due to the unstable performance of the MDC reactor. The variation of CE and energy harvested rate obtained during the steady state operation are shown in Fig. 5. The CE percentage in the continuously operated MDC reached 45% during
The first 10 days (data are not shown) and then remained relatively stable until the end of operation (Fig. 5A). The CE in the MDC operating under repeated batch cycles decreased gradually from 94 to 74% within the same time (Fig. 5B). The obtained results showed a higher CE percentage compared to previously reported three-chamber MDCs [26]. The high amount of CE obtained in this study indicated that COD removal in the anode chamber was mostly used for current generation. The maximum energy harvest rate during continuous operation was relatively constant at a value of 1.75 C.h⁻¹. In the batch MDC, when the solutions were replaced, the average energy harvest rate fluctuated between 0.46 to 0.93 C.h⁻¹ during every single batch cycle. The very different pattern for electron harvest rate variation in MDC reactors is due to different amounts of available substrate for the anodic bacteria. The amount of CR indicated a higher value for the batch MDC compared to the continuously fed MDC. An average CR of 35% was produced at the continuously-fed MDC, while it was 29.9 and 55.6% during the first and second day of operation for the MDC operated in batch mode. The obtained results for CR and rate of harvested energy were significantly higher than the photosynthetic MDC operated in fed-batch condition [30]. The main reason for the high coulombs obtained in this study was the availability of oxygen as an electron acceptor in the cathode chamber and the high biodegradability of the anolyte solution.

3.4. Desalination performance

In order to compare the salt removal performance in the batch and continuously operated MDC, the conductivity of the salt solution was measured during operation. The solution conductivity and salt removal over a typical desalination cycle is demonstrated in Fig. 6. According to presented data, the salt solution conductivity decreased gradually in both MDCs over a two day desalination cycle. During the first 36 h of operation, the salt removal rate was higher in the batch MDC compared to the continuously fed MDC during repeated batch desalination cycles.
MDC. Afterward, interestingly, salt removal in the continuous MDC overtook the batch MDC, likely due to significant reduction of produced current during operation under batch mode. The conductivity of the salt solution in the batch MDC decreased from an initial salt concentration of 54.5 ± 0.64 to 26.8 ± 0.73 and 17.4 ± 0.78 mS.cm⁻¹ during the first and second day of the batch cycle, respectively. The corresponding data for the continuously fed MDC were 31.8 and 10.9 mS.cm⁻¹, respectively. Based on the change in conductivity of salt solution, the final salt removal in a single desalination cycle by the MDCs under batch and continuous condition had an average amount of 68.1% and 80%, respectively. The higher salt removal rate in the continuously operated MDC is mainly attributed to the higher power and current generation during each desalination cycle. These salt removals were lower than those previously obtained by Cao et al. [14] in a three-chamber MDC using ferricyanide catholyte. However, obtained data are comparable to those reported by Meng et al. [31] using dewatered sludge as fuel. In their work, desalination reached 29 and 67% after 72 h and 42 day operation, respectively, using a 35 g.L⁻¹ NaCl solution.

4. Conclusions

In this study, energy was generated from municipal wastewater along with water desalination in a batch and continuously operated microbial desalination cell. A maximum power density of 15.9 W.m⁻³ with an average columbic efficiency of 42.8% was obtained in the continuously fed MDC. It also achieved up to a 80% salt removal rate and removed more than 83.7% of organic matters during the operation. The batch MDC produced the maximum power density, desalination rate and COD removal of 13.9 W.m⁻³, 68.1% and 69.9%, respectively. These results indicate that the type of hydraulic flow can affect the performance of a MDC. But further investigation would be necessary to evaluate the cost of these operational conditions in order to make a final decision. The results and experiences obtained from this study will enable us to improve the performance of the MDC for both desalination and wastewater treatment.

References


