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Simultaneous Electricity Generation and Sulfur Removal by Electrogenic Sulfate Reducing Bacteria in BES System

Tahmineh Taheri Dezfouli[a], Reza Marandi[b*], Morteza Kashefiolasl[b], Mozhgan Emtyazjoo[c], Maasomeh Javaheri[d]

[a] *Department of Environment, Islamic Azad University, North Tehran Branch, Tehran, Iran.*
[b] *Department of Environmental Engineering, Islamic Azad University, North Tehran Branch, Tehran, Iran.*
[c] *Department of Marine Sciences, Islamic Azad University, North Tehran Branch, Tehran, Iran.*
[d] *Department of Ceramics, Materials and Energy Research Center (MERC), MeshkinDasht, Alborz, Iran.*

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ABSTRACT

The modern BioElectrochemical technologies can convert the energy stored in the chemical bonds of biodegradable organic materials to renewable electrical energy through the catalytic reactions of microorganisms while treating the waste waters. The present research was conducted to evaluate the efficiency of a single-chamber Bioelectrochemical system with the carbon aerogel catalyst, as a simple and inexpensive method, in removing the corrosive and odorous sulfur compounds from municipal wastewater simultaneously with electricity generation by using indigenous bacterial consortium. The used bacteria were isolated from local lagoon sediments, and the municipal wastewater was used as the substrate. During six months of the Bioelectrochemical cell operation, the sulfate concentration was dropped to a minimum of 63 ± 57.2 mg/l, indicating the ability of the system to remove 71.8 % of the sulfate from the municipal wastewater and the production of bioenergy. With a 304 mV Open Circulate voltage, the maximum removal of Chemical Oxygen Demand was 80 % and the maximum power density was 1.82 mW/m^2. Carbon aerogel, as a novel material with suitable absorbance and resistance to oxidation at urban wastewater pH, can be, therefore, coated on electrodes to facilitate the Oxidation Reduction Reactions and electricity transmission. The existence of elemental sulfur in the sediments showed that these systems could be optimized to recover the elemental sulfur from the municipal wastewater.

1. INTRODUCTION

Increasing the consumption of fossil fuels has led to irreparable consequences for the planet´s environment, forcing countries to find renewable energy sources with low carbon foot print [1]. Nowadays, BioElectrochemical technologies have attracted much attention in treating wastewaters and obtaining renewable energy from biodegradable organic matters[2–5]. The energy stored in the chemical bonds of organic matters is converted to electrical energy through the catalytic reactions of microorganisms[1,4,6–8]. Basically, these technologies operate based on the intrinsic ability of the bacteria to supply their required energy while transferring electrons from the substrate to an electron acceptor with a higher redox potential. The bacteria in these cells are forced to transfer the electrons to the electrodes that transfer the electrons to the external circuit [3,9,10]. Different types of Bioelectrochemical systems(BESs) including Microbial Fuel Cells (MFCs), Microbial Electrolysis Cells (MECs) and Microbial Desalination Cells (MDCs) [7], can be employed to treat the wastewaters, to produce valuable products through electrochemical or electrosynthetic reactions or as the power supply of the remote sensors [7,11].

Different types of materials have been employed as the substrate and electron acceptors in BESs (Table 1); these include dissolved sulfate[10]. The application of a substrate like wastewater as the electron source is interesting because the demand for water or wastewater treatment systems with a low carbon footprint is rising [7,12]. As for the BES´s, the purpose is to remove organic carbon; however, a mixture substrate such as wastewater contains some other compounds such as nitrogen and sulfur [3].

The sulfate present in the wastewater is generally converted to sulfide by sulfate-reducing bacteria (SRB) in the anaerobic conditions [20,21]. In this system, the SRB´s oxidize organic matters (including acetate, lactate, butyrate, etc.) and reduce the sulfate ions, as presented in the following reaction [10].

$$(CH_2\,O)_n + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^- \quad (1)$$

Sulfides can work as an electron carrier from the bacteria to electron acceptors such as Fe (Ⅲ) oxides [3] and act as an intermediate reducing agent. The released protons can be reduced by oxygen in the cathode; in the standard conditions, sulfide can be converted to the elemental S^o by sulfur-oxidizing bacteria from sulfide (SOB) in potentials higher than 0.274, compared to the Standard Hydrogen Electrode (SHE). If the potential increases, S can be oxidized to sulfate again, which cannot be reduced again by anodic biofilm microorganisms [10,21,22]. In single-chamber air cathode MFCs, sulfate can be reduced to S$^\circ$ according to the Equation 2; the deposited S$^\circ$ results in electrodes clogging and the reduction of electricity generation [8].

$$SO_4^{2-} + 8H^+ + 6e^- \rightarrow S^\circ + 4H_2O \quad (2)$$

Thiobacilluses are known as chemoautotrophs that can potentiate the anaerobic oxidation of sulfur by reducing Fe (Ⅲ) or nitrate as the final electron receptor [22].

*Corresponding Author's Email: rmarandi@uoguelph.ca (R. Marandi)

Table 1. Comparison of the substrate and catalyst, and the results of the similar researches conducted on single chamber BES´s.

Substrate	Inoculation	Power density (mw/m^2)	Catalyst	Ref.
Synthetic wastewater	Sludge suspended microorganisms	9.33	Carbon cloth (0.5 Mg. /cm^2 Pt loading)	[13]
		1.53 and 1.36	Carbon-fiber-felt, TiO_2 and Fe_2O_3 nano sheets	[14]
Nitrate sulfate	Mixed culture	14.0 mW/m^2		[15]
Domestic wastewater		5.24 ± 20	Acticated carbon (AC) and carbon black (CB)	[16]
Acetate fuel	Geobacter spp	1.36 ± 0.20	AC + platinum	[17]
Acid mine drainage	Mixed culture	57 ± 11 A/m^2 (current density reported)	Multiwall nanotube/carbon granule	[18]
Sodium acetate	The effluent of MFCs that operated for over one year.	2300	Carbon Aerogel Air Cathodes	[5]
Glucose + pre-treatment wastewater (FGPW)	SRB	28.12 mA/m^2 (current density reported)	Carbon cloth	[19]
Modified culture medium of Postage	Mixed culture of sulfate-reducing bacteria	0.68	Potassium ferricyanide	[10]
Modified M9 medium	Aerobic sulfide oxidize bacteria	47 Wm^{-3}	Hegsacyanoferrat, granular graphite	[3]

The study conducted by Zhao et al. [23] on the activated carbon coating anode used to remove sulfate in a microbial fuel cell showed that the application of the SRB (Desulfovibrio desulfuricans) made it possible to generate electricity in an MFC and remove 99 % of the sulfate simultaneously. This approach is based on the non-oxidative reduction of sulfide produced by D. desulfuricans in the anode. In addition to sulfide, some other compounds such as Fe^{2+}, Cysteine and AHQDs can act as the electron carrier, where the difference in electricity generation depends on their oxidation and reduction abilities to processes [18,22]. The greater the concentration of the electron carrier on the anodic side is, the more electricity will be produced. Electricity generation in the system can show the amount of produced sulfide [20]. In similar studies, up to 101 mV electricity has been observed, resulting from the oxidation of sulfide and the removal of 98 % of sulfide, that is equal to 514 mg per day [3,11,18].

Despite the remarkable ability of these systems for the direct conversion of organic matter in wastewater to electricity, there are many factors that limit their practical application [6,11]. The most important factor is the poor kinetic oxidation reduction reactions (ORR) at the neutral pH required for the single chamber air cathode cells [5]. Enhancing the catalyst efficiency of this pathway can contribute to the better performance of the system. Many studies have been carried out on various metallic and nonmetallic catalysts [5,21], in which carbon materials are more widely considered for their specific surface area and chemical inactivity as the catalyst base. Therefore, classical carbon foundations such as activated carbon, carbon black, graphite and graphite-like materials have been widely studied [24].

Recently, the sol-gel of resorcinol-formaldehyde has been widely considered. The synthesis of these sol-gels, which is carried out with a hydrolysis-condensation mechanism, is similar to that of inorganic sol-gels. This method can be used to synthesize carbonic and organic aerogels and xerogels [25]. They can be used in numerous applications such as catalysts, adsorbents and electrochemical energy storage devices [25]. The properties of these aerogels include high hierarchical porosity (> 80 %), high specific surface area (400-1200 m^2/g) and high total pore volume (TPV), depending largely on the synthesis and the condition of the process. The high electro catalytic activity and selectivity that can facilitate ORR in the air cathode in the neutral pH electrolyte have been demonstrated [5]. These structures are charactrerized by low thermal conductivity due to their high porosity. Their nano particle structure also controls their behavior as electrodes in electrochemical double- layer capacitors [24,25].

The objective of the present study is to examine the efficiency of a single-chamber BES system with carbon aerogel coated cathode, as a new, simple and inexpensive method, to remove the corrosive and odorous sulfur compounds from municipal wastewater, as a renewable energy source by using the native bacteria.

2. MATERIALS AND METHODS

2.1. Isolation and culture of electrogen sulfate reductase bacteria

The anaerobic sediments from Anzali Lagoon (37°27'51.7"N 49°28'19.0"E) and Eshgh Abad area of the Varamin County (35.4592169, 51.4542183) were collected; with a ratio of 1:1, they were cultured under both aerobic and anaerobic conditions in Luria-Bertani (LB) and BHl nutrient medium in an incubator at a temperature of 35.5 ºC [26].The mixed culture was incubated for bacterial growth and coexistance for two monthes and fed every 4 days. The dilution and formation of the bacterial suspension to inoculate the cell were performed for the aerobic types after 48 hours; the same was

repeated for the anaerobic types after 96 hours. This solution was used in a pilot cell, allowing the microorganisms to grow for 10 days.

2.2. Design and starting up microbial fuel cell on a lab scale

In the laboratory phase, a cylindrical glass chamber with a capacity of 1500 ml with a cylindrical anode at a distance of 6 cm around the tubular air cathode was used. Since the anaerobic bacteria grow at a very slow rate, the pilot was designed in the laboratory as a sequencing batch reactor (SBR) to prevent the biofilms from being rinsed. The structure of single-chamber cell electrodes of air cathode was created based on a method developed by Cheng et al. [27].

The 200 gr/m^2 (ISO3374) double-sided carbon cloth made by Iran Composite with a width of 0.2 mm as the electrode and stainless steel mesh (grade 304) was used as an electricity collector. The materials used as the cathode in the microbial fuel cells are the same as those in the anode, except that when these materials are used in the cathode, usually there is usually also a need for a catalyst [5,12]. Since the microorganisms can act as the biocatalyst in the cathode and speed up the transfer and consumption of electrons, the present study was conducted without any mediator [28,29]. To increase the cathode surface area and facilitate ORR, a layer of carbon aerogel from a previous study was coated on the cathode as the catalyst base [5,24]. To complete the wastewater treatment process, an aeration chamber was placed on the effluent of the cell (Figure.1).

The municipal wastewater from Ekbatan wastewater treatment plant (Tehran,Iran) with a 7.81 average influent pH,1120 µs/ cm conductivity, 677.23 mg/l COD and 224 mg/l sulfate was used as the substrate.

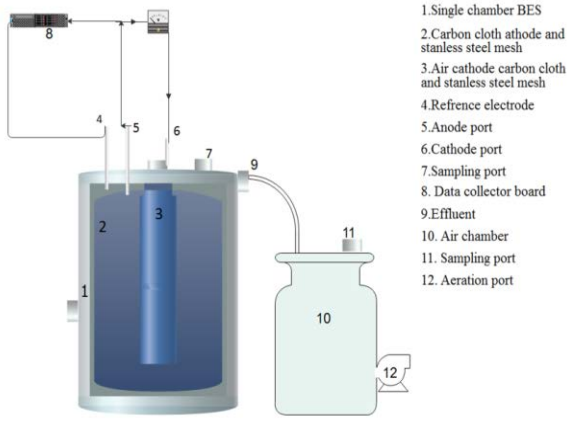


Figure 1. Schematic of the designed BES.

2.3. Methods of analysis

The inoculum was added to the cell with two concentrations of 0.5 and 10 McFarland to examine the effects of the presence of the microorganisms on the process of electricity generation. The effects of key parameters and the optimum conditions, were examined using the RSM method by Design Expert11. Some instances of the input and output of the system were collected to measure COD, sulfate and sulfide at the intervals of 1.5, 3, 24, 7, 48 and 72 hours.The concentrations were analyzed by the standard method (APHA, 2011) [30]. Each test was repeated twice. The cell voltage was recorded by the multimeter (mastec, mas830L.china) every ten minutes and a new feed (wastewater) was added to the cell whenever the voltage went below 50 mV(4).

The current (I=V/R) and power (P=IV) were set according to the Ohm's law, power density (Pd=IV/A), where A is the area of the operational surface. Coulombic Efficiency (CE) was drawn based on the method proposed by Chen et al. [31]; further, the polarization curve was obtained by applying the external resistance from 2000 Ω to 10 Ω at 10 minute interval untill reaching a constant voltage. The internal resistance and the maximum power density were obtained by analyzing the polarization curve [4]. The electrochemical tests were conducted by Potentiostat (ilium stat. XRE. ILUM technology) with the referenced electrode Ag/AgCl in the potential range of 4 mV to -4 at a scan rate of 10 mV/s. The morphology and structure of the biofilm were observed by the Scanning Electron Microscopy (SEM S360, Cambridge 1990).

3. RESULTS AND DISCUSSION

3.1. Electricity generation and growth kinetic of the bacteria

The first step in the present research is to choose a proper microbial source in the optimum thermal conditions to provide appropriate conditions for the active biocatalyst microorganisms to create a steady state by the mixed culture. The mixtures of aerobic and anaerobic bacteria from the sediment microbial cell electrodes were inoculated into the culture medium as two separate microbial sources; sampling was performed every 2 hours and light absorption of the samples was determined at 620 nm. The results of the growth kinetics of the aerobic and anaerobic mixtures at ambient temperature (25 °C) were obtained, as shown in Figure 2 (Figure 2).

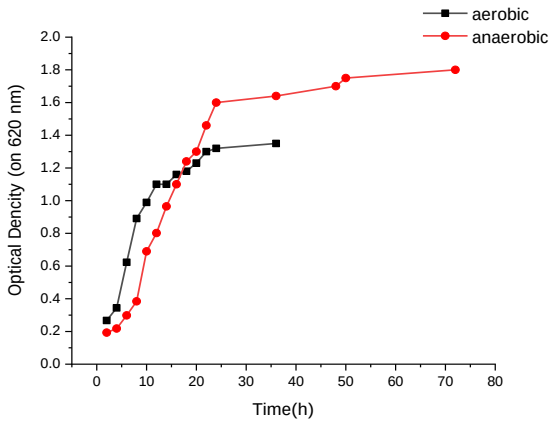


Figure 2. Growth diagram of the aerobic and anaerobic bacteria isolated as inoculums from the SMFC electrodes (optical absorption of the samples was determined at 620 nm).

According to what was observed earlier, the lag phase of the aerobic species was up to 2 hours; however, it was 6 hours for the anaerobic types. Then, the log phase was observed. In the first 8 hours, the aerobic microorganisms peaked, while the anaerobic types grew more slowly. The aerobic bacteria entered the stationary state after 20 hours. Due to the single-chamber structure of the cell and the rapid growth of bacteria in the anaerobic condition , the studied mixed culture bacteria were probably facultative anaerobic species that grew under low oxygen content of the cell.

The possibility of using a microbial source as the inoculum in the BES cell and electricity generation was evaluated and the proper growth of the given microbial source in the environmental conditions was also investigated. Figure 3a shows the electricity generated when the cell started to operate in an open circulate situation. The voltage generation was working very slowly and at a low level during the first three days when the cell started to operate. The whole process was monitored from the beginning, and a constant voltage as large as the voltage for five times of rebuilding the system was observed after five to seven days. Each time the cell was fed, a sudden drop in the voltage occured (on average, from 53 mV to 11 mV) and peaked afterward. A decrease in pH at each run was observed along with an increase in the voltage (from 7.6 to 6.8, on average). The highest voltage was observed at a lower pH. The maximum generated voltage was 304 mV (Figure 3b).

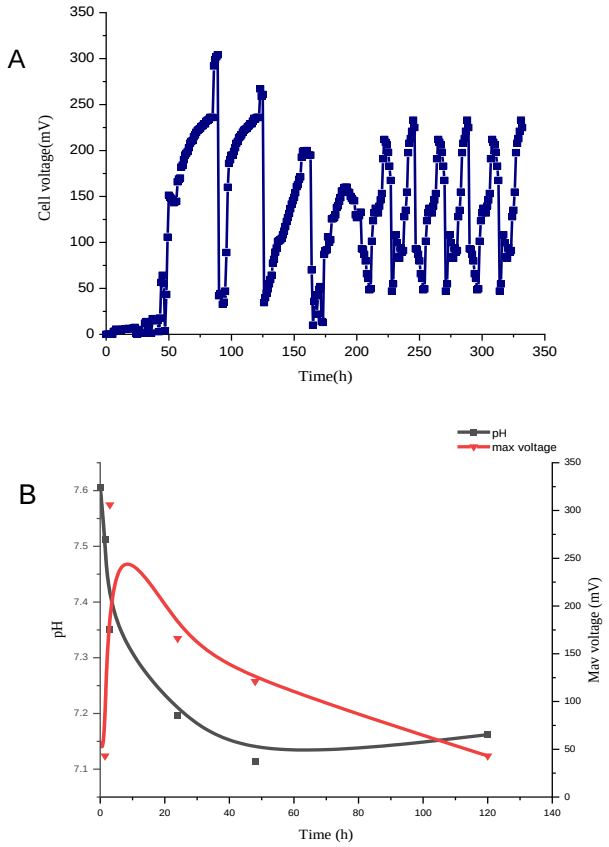


Figure 3. a) The single-chamber air-cathode BES cell's open circulate voltage curve based on time, b) Voltage variation curve and pH in a 120 hour operation cycle.

The voltage rises for 72 hours; then a sudden increase in voltage (probably because of consuming acetate for generating electricity) was observed that was followed by a reduction in voltage that resulted from the organic substrate in the cell (Figure 3b).

Based on the growth kinetics of bacteria (methanogens and sulfate reductases), it could be concluded that using the bacterial consortium enabled the system to make the full use of the compounds in the wastewater to generate electricity. A sudden drop in the voltage curve and the increase after each feeding of the cell indicated that electricity generation was affected by the chemical reactions. The initial voltage drop (activation over- potential) indicated the energy consumption required to activate the oxidation and reduction reactions in the cathode and anode, respectively; in fact the lower the pH in air-cathode reactors, the greater the H^+ provided for the cathodic reduction reaction. A decrease in pH at each run was observed along with an increase in the voltage. According to Zhang et al. [5], a decrease in the maximum current after some system operation could result from the development of biofilm on the cathode and its effect on the catalytic activity of carbon.

The maximum generated voltage was 304 mV, which could be compared with the previous findings [8]. The results, as shown in Figure 3, revealed that electricity was generated by the organic compounds of the municipal wastewater sediments as the substrate without using the activation current; therefore, BES could enter the municipal wastewater system without any auxiliary devices.

3.2. Effect of microbial consortium and optimum condition on cell performance

In two separate experiments, two inoculum concentrations of 0.5 and 10 McFarland were examined. A mixed culture in each experiment was inoculated to the LB culture medium as the inoculum, and the current and power generation of the cell were studied (Figure 4). The maximum current density at the concentration of 0.5 McF was 2.26 mA/m^2, in which the cell stopped working after a while. The maximum current in Cell 2 with a higher microbial concentration was 2.1 ± 0.65 mA, while the maximum current generation in Cell 1 was 0.976 ± 0.31 mA. As shown in Figure 4, although the inoculation concentration did not make a significant difference in the power generation, the 10 McF concentration had the greatest power generation (0.54 mW/m^2) (Figure 5).

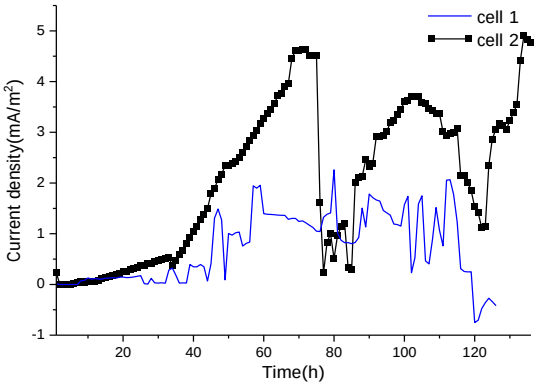


Figure 4. Comparison of the current density of two single-chamber BES over time (120 hours) at inoculum concentrations of 0.5 McF (Cell 1) and 10 McF (Cell 2).

The comparison results of the effect of microorganism concentration on the cell performance showed that the microorganisms required for performing the biocatalytic activities in the anodic chamber were not provided in 0.5 McF inoculations, leading to a decrease in power generation. In high percentage inoculations (10 McF concentration), although the microorganisms required for performing the intended reaction in the anodic chamber were provided, the microbial assembly in the anodic chamber decreased the mass transfer, resulting in a decrease in power generation [6,22].

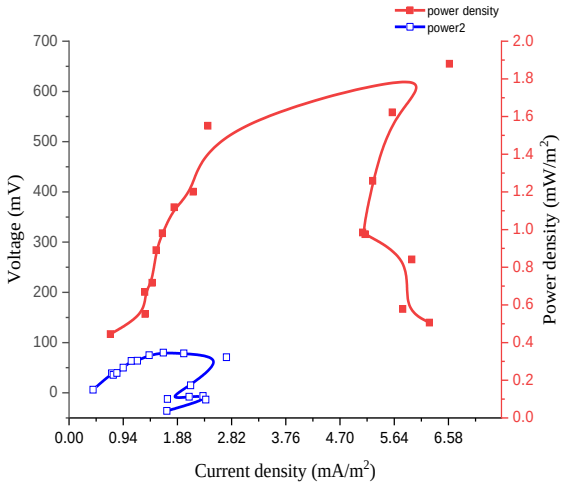


Figure 5. Comparison of the current and power density of two systems at inoculum concentrations of 0.5 McF (pd 1) and 10 McF (pd2) to study the effect of microbial mixed culture on cell performance after steady state (p<. 05).

The effects of key parameters and the optimum conditions for COD and sulfour removal , were examined using the RSM method. The Hydraulic Retention Time was 40 hours at the neutral pH and the optimal ambient temperature (22 ºC) was determined (Table 2).

Table 2. RSM method results of optimum conditions for COD and sulfour removal by single-chamber BESs.

Desirability	0.870
TDS (mg/l)	503.608 ± 87.8599
BOD(mg/l)	61.669 ± 117.734
COD (mg/l)	94.001 ± 157.998
S^{2-} (mg/l)	288.144 ± 37.5079
SO_4 (mg/l)	82.380 ± 57.1872
Tem (˚C)	22.330
HRT (h)	40.622
pH	7.107

3.3. Simultaneous sulfur removal and electricity production

The time-based changes in sulfate and sulfide concentrations are illustrated in Figure 6. The sulfate concentration decreased by 52 % during the first three hours (from 224 mg/l to 84 ± 57.2 mg/l); then, they remained constant till the end of the operating period. The sulfide concentration increased over the first 24 hours to a maximum of 332 ± 34.96 mg/l; subsequently, a reduction in the dissolved sulfide concentration was observed in the cell. The reduction of concentration probably stemmed from the fact that the sulfide concentration reached 332 ± 37.5 mg/l; this is a range that can restrict the activity of microorganisms (in these cases, SRB bacteria) based on the references [12, 30]. A weak negative correlation was also observed between the concentration of sulfur compounds and the retention time (p<. 05).

The time-based changes in sulfate and sulfide concentrations also indicated the limitation of sulfate-reducing bacteria in converting sulfate to sulfide. This could be due to the increase of the reduction potential of the iron-reducing bacteria that played an important role in generating electricity according to the previous research [8]. The sulfide concentration increased over the first 24 hours; according to Pozo et al. [18], this may indicate the activity of electrogen sulfate reductase bacteria of anode and the autotrophic reduction of sulfate in BES systems.

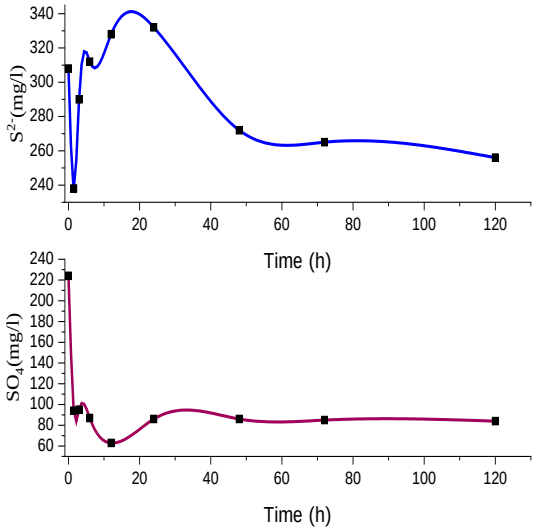
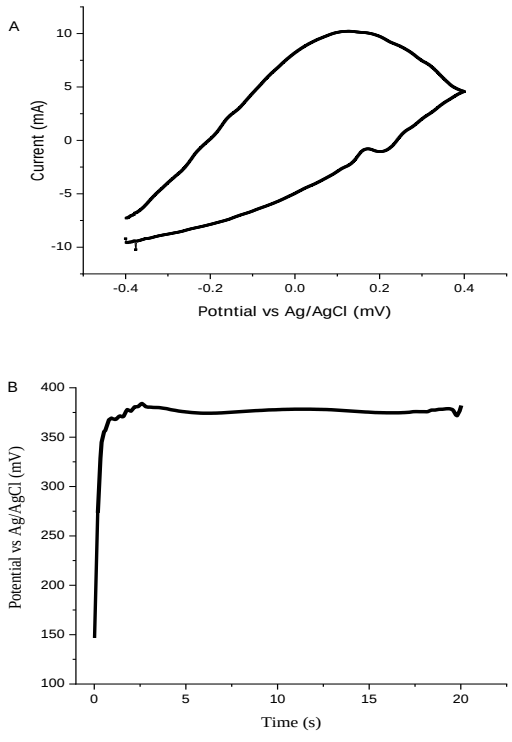


Figure 6. Examination of the changes in the concentrations of dissolved sulfate and sulfide in the wastewater during 120 hours of the cell operation.

The electrochemical tests were conducted to explore the kinetics of the cathodic oxygen reduction reaction (ORR), and two peaks were observed on the LSV curve at 1.7 and -1.3 mV vs. Ag/AgCl (vs. SHE). Then, they presented a reduction in oxygen and sulfur in the aerobic cathode as the final acceptor in comparison to the redox table [31]. The reduction peaks were also observed on the CV curve and the reactions in this potential range were considered to be complete forward and backward reactions. The chronopotentiometry curve in the first 20 seconds of these two reactions revealed the adjacent reduction cathode (Figure 7).



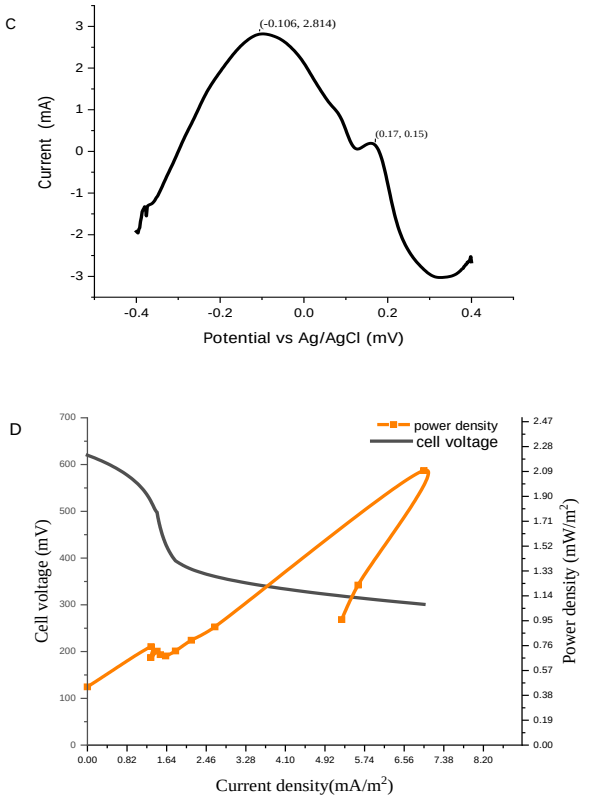


Figure 7. Potentiometric curves of the aerobic bio-cathode with carbon aerogel at -0.4 - 0.4 mV (vs Ag/AgCl) potential: a) CV curve, b) Potentiometric curve, c) LSV Curve , and d) Polarization curve of BES in the batch mode.

The maximum generated voltage was 304 mV. The low operation voltage (Vop) in relation to the predicted thermodynamic potential (E_{thermo}) may originate from different factors such as the reactions activation-related losses in the electrodes and the transfer of electrons to the anode, metabolism of bacteria, losses of mass transfer (due to the finite flux from the reactors to the electrodes), and the ohmic losses resulting from the resistance to the proton release and resistance against charge transfer [32]. The square shape of the CV curve indicated the good catalytic activity of carbon aerogel as a high-porosity, high-surface area and a high electrical conductivity catalyst base, on the aerobic cathode, leading to the acceleration of the reduction reactions [5] and the sufficient existence of oxygen as the final receptor of protons. The peaks observed in the oxidation curve of carbon aerogel cathode represent water as an ORR product, which implies the 4 proton path for oxidation in the cathode (O_2 $+4H^+ +4e$ _ $2H_2O$) [5].

After 30 days of operation, the amounts of sulfur in the anaerobic cell sediments and the aeration chamber sludge were examined by the carbon/sulfur determination device (cs Eltra 2000-Germany) to determine the existence of the elemental sulfur as a result of the conversion of sulfide to sulfur. The total sediment volume was 50 and 70 ml for the cell effluent and Aeration chamber, respectively. The sediments were allowed to be dried at room temperature and weighted before elemental sulfur measurement. According to Table 3, sulfur was recovered as an element from the sludge; this indicated the activity of the sulfide-oxidizing bacteria of the air cathode. Although the quantity of sulfur in cell sludge was low, its weight percent was higher.

A piece of each electrode (1*1 cm) was analyzed by SEM after the operation for a period of time. The SEM images demonstrate the biotic biofilm formation and its good microbial attachment to the air cathode of BES (Figure 8). Long rod-shape bacteria (about 5.00 µm in the length) and other coccial bacteria could be observed upon the close examination of the cathode. These bacteria were similar to sulfide-oxidizing bacteria of the air cathode in previous studies [40].

Table 3. The amount of the elemental sulfur in the cell sediments and the aeration chamber (determination of S leached from the air cathode).

	Total sediment vol. (ml)	**Dehydrate sediment weight (mg)**	**Sulfur weight percent (%)**
Anaerobic cell	50	143	1.85
Aeration chamber	70	189	1.53

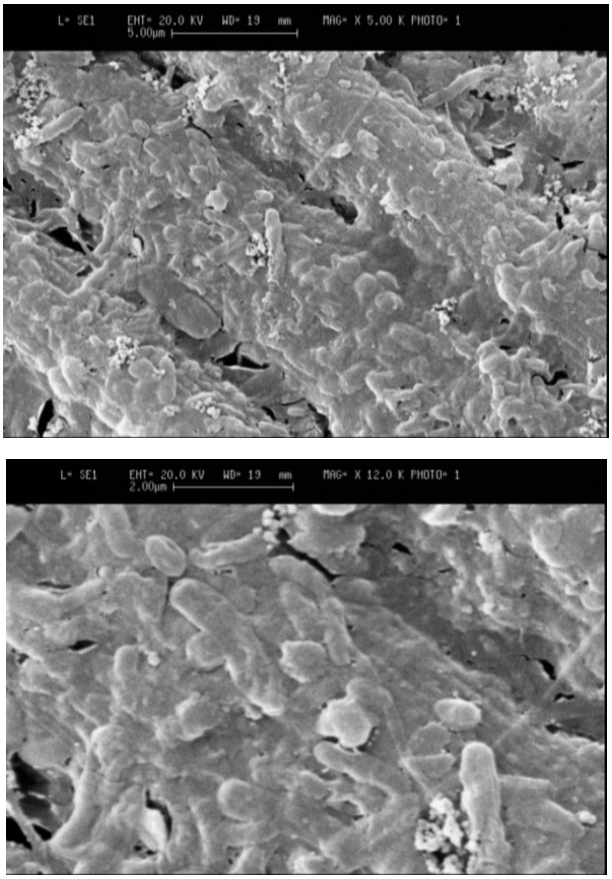


Figure 8. SEM images of air cathode, biofilm formation and microbe attachment to the carbon aerogel air cathode and cathode compartment, showing long rod-shaped bacteria.

The microorganisms were finely settled on the electrodes and biofilms formed on each cathode and anode, as compared to the recent studies [5,13].

The wastewater treatment efficiency of the BES system is shown in Table 4. According to the results, the final effluent concentration of COD and sulfate could meet Iran's Environmental Protection Organization Standard for the agricultural reuse, but the sulfid concentration can not (COD, Sulfate and sulfide lower than 200 mg/l, 500 mg/l and 3 mg/l, respectively).

Figure 9 shows the correlation between sulfate removal and electricity generation over a 72 hour period of the operation of the cell, revealing that the sulfate concentration was decreased by 58 % through increasing the current generation up to 3.4 mA; on the other hand, the sulfide concentration was increased simultaneously. Thus, it could be concluded that the sulfate was removed by being reduced to sulfide and the concentration of the removed sulfate was involved in generating voltage up to the concentration range of 84 ± 57.2 mg/l.

Table 4. The average values of COD, BOD, sulfate and sulfide removal efficiency of BES from wastewater.

	COD (mg/l)	BOD	SO_4^{2-} (mg/l)	S^{2-} (mg/l)	Turbidity (NTU)
Influent	677.23 ± 157.998	353.12 ± 117.734	224 ± 57.2	308 ± 37.5	160 ± 31.415
Anaerobic cell effluent	150 ± 157.998	97.89 ± 117.734	63 ± 57.2	332 ± 37.5	60 ± 31.415
Aeration chamber	95 ± 157.998	67.1 ± 117.734	82 ± 57.2	256 ± 37.5	14.2 ± 31.415
Removal efficiency (%)	80.46	80.52	71.8	16.5	97

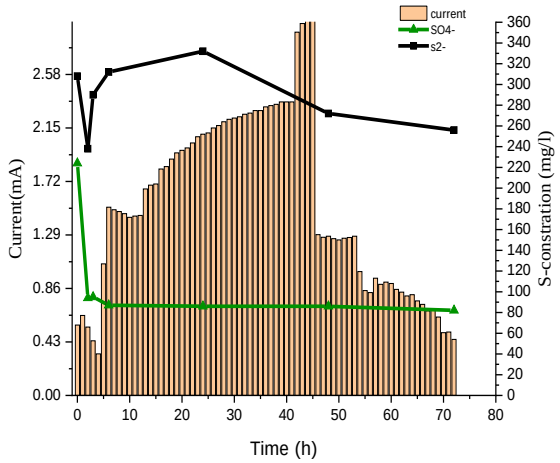


Figure 9. Correlation between electricity generation and change in sulfate and sulfide concentrations in the air cathode single chamber BES cell.

By observing the correlation between sulfate removal and electricity generated over a 72 hour period of the cell operation, the sulfate concentration decreased when the current generation increased; however, the measured sulfide was not increased to the same degree because it could turn into gaseous hydrogen sulfide and other sulfur compounds quickly [20]. Thus, it could be concluded that the sulfate was removed by being reduced to sulfide and the concentration of the removed sulfate was involved in generating voltage up to the concentration range of 84 ± 57.2 mg/l. After reaching this concentration, a severe reduction in the electricity and stabilization of sulfate concentration was observed, probably because of the limitation of the SRB bacteria as a result of an increase in the sulfide concentration or the domination of the methanogens activites.

Sulfate concentration increased from the initial concentration of 224 mg/l to 63 ± 57.2 mg/l, showing the ability of the system to remove 71.8 % of the sulfate from the municipal wastewater and the production of bioenergy. The maximum removal of COD was 80 % and the maximum power density was 54 mW/cm^3 and 1.82 mW/cm^2, similar to the results obtained by Niyom et al. [33]. These results could be acceptable given the use of municipal wastewater instead of the synthetic wastewater employed in most of the previous research studies and varied microbial consortiums. Since the ratio COD: $SO4^{2-}$ could affect the microbial performance of MFCs, this ratio must also influence the performance of treatment and electricity generation [34]. The maximum removal of the total COD in this study was 95 ± 53.7 mg/l, where the ratio of COD: $SO4^{-}$ was finalized as 1.1. The previous studies have also shown that Methanogens could dominate SRBs when this ratio is greater than 2 (like the first two hours of the cell performance). However, when this ratio is less than 1.3, SRBs are the dominant bacteria [35,36].

The existence of the elemental sulfur in the cell sediments was consistent with the findings of some previous studies [3,8]. Sulfide concentration was involved in the increase of the voltage, as shown in the previous studies [18]. This correlation proved that electricity generation in a microbial fuel cell with wastewater as a renewable energy source, could remove the sulfur compounds or control them in the wastewater treatment system.

4. CONCLUSIONS

According to the increasing demand for renewable energy sources, municipal wastewater can be used as an inexpensive and affordable source of renewable energy. The present study investigated the efficiency of electricity generation by removing sulfur compounds or controlling them through a single chamber BES and, also the possibility of extracting elemental sulfur from municipal wastewater.

The results, therefore, revealed that electricity generation in this BES could remove 71.8 % of the sulfur compounds from wastewater treatment and that the sulfate concentration was dropped to a minimum of 63 ± 57.2 mg/l. Electricity was generated by microorganisms as biocatalysts from the organic compounds of the municipal wastewater without applying an activation current. With a 304 mV Open Circulate Voltage, the maximum removal of Chemical Oxygen Demand was 80 % and the maximum power density was 1.82 mW/m^2. Carbon aerogel, as a novel material with suitable absorption and disintegration abilities for reactive substances is resistant to oxidation at the urban wastewater pH; therefore, it could be used on electrodes to facilitate the reactions and electricity transmission.

Such instruments could be used in municipal wastewater systems such as manholes, rainwater harvesting canals and sewers, without any auxiliary devices. The existence of the elemental sulfur in cell sediments was consistent, indicating that these systems could be optimized to recover the elemental sulfur from the municipal or industrial wastewaters.

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NOMENCLATURE

A	Area
AC	Activated carbon
BHI	Brain heart infusion
BES	Bio electrochemical system
CB	Carbon black
CE	Colombic efficiency
COD	Chemical oxygen demand
I	Current
LB	Luria-Bertani
MFC	Microbial fuel cell
ORR	Oxidation reduction reactions
OCP	Open circulate voltage
Pd	Power density
P	Power
R	Resistance
SHE	Standard hydrogen electrode
SOB	Sulfur oxidizing bacteria
SBR	Sequencing batch reactor
SEM	Scanning electron microscope
TPV	Total pore volume

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