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Bioelectrochemical treatment of olive oil mill wastewater using an optimized microbial electrolysis cell to produce hydrogen

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Abstract−A single chamber microbial electrolysis cell (MEC) was constructed to treat olive oil mill wastewater (OOMW) biologically and produce hydrogen simultaneously. To characterize the optimal MEC condition, the MEC was fed with synthetic wastewater (SW) having a phenol concentration of 250 mg l^{-1}. Therefore, the influence of different applied voltages and cathode materials was explored and the optimum condition for MEC was determined, which was when the stainless steel cathode was implemented and the external voltage of 0.6 V was supplied. Chemical oxygen demand (COD) removal of 62% and current density of 362 mA m^{-2} were obtained for OOMW treatment, while COD removal of 73% and the current density of 274.4 mA m^{-2} were attained for SW treatment in this MEC at 0.6 V. Hydrogen production rate was 0.045 m^3 H_2 $m^{-3}d^{-1}$ for SW and 0.053 m^3 H_2 $m^{-3}d^{-1}$ for OOMW. Furthermore, the coulombic efficiency and cathodic hydrogen recovery were 23% and 81%, respectively. Finally, MEC performance in terms of electrical current generation, wastewater treatment and hydrogen production was compared to some similar reported studies.

Keywords: Hydrogen Production, Olive Oil Mill Wastewater, Microbial Electrolysis Cell, Wastewater Treatment, Phenol

INTRODUCTION

Olive oil mill wastewater (OOMW) is produced during the mechanical procedures of manufacturing olive oil. OOMW contains high concentrations of organic components, including sugars, phenolic compounds, organic acids, polyalcohol, pectin and oil [1,2]. Since the yearly OOMW production is roughly calculated to be about 5.4×10^6 m^3 [3], its treatment has become a significant environmental issue in the Mediterranean countries [4] and other non-traditional producing countries such as Australia and South America [3].

Among different wastewater treatment techniques, the biological treatment is gaining considerable interest due to its low cost and clean nature [5]. So, the biological treatment of OOMW has been a subject of many studies; for instance, Isidori et al. achieved maximum organic content removal of 85% in OOMW treatment by utilizing the commercial mixed bacterial consortium [6]. Fiorentino et al. [7] gathered the OOMW in southern Italy and treated it by different methods, including the chemical oxidative method with $FeCl_3$ and a biotreatment which was carried out in a pilot plant in presence of commercial bacteria. They came to the conclusion that by using the combination of these two methods, more removal could be attained. Moreover, Bagheri et al. inoculated a microbial fuel cell (MFC) with activated sludge and *Ralstonia eutropha* pure culture to treat OOMW and reached a power density of 7.8 mW m^{-2} [8].

The microbial electrolysis cell (MEC) is a bioelectrochemical system that can mineralize organic content by use of anaerobic bacteria to produce current density and biogas such as methane or hydrogen [9,10]. The usual configurations of MECs are double chamber and single chamber. A single chamber MEC is only composed of the anode chamber, but the double chamber consists of anodic and cathodic compartments. So far, many single chamber MECs have been applied with numerous configurations and characteristics to treat wastewaters (such as the work of Liu et al. and Rani et al. [11,12]) and produce hydrogen (like the research by Cebecioglu et al. and Cui et al. [13,14]).

Hydrogen is a suitable energy carrier because of its large density, high reaction rate and clean oxidation which forms water [10,15, 16]. Most conventional methods to produce hydrogen are microbial fermentation, electrolysis of water and hydrocarbon reforming [17]. Producing sustainable hydrogen gas by microorganisms is an eagerly awaited technology leading to gradually diminishing of the use of fossil fuels by utilizing its alternative. Hydrogen generation by MEC is counted as an innovative technology which can be preferred to other techniques due to its minimum energy requirement and environmentally friendly basis [18,19].

In this study, the anaerobic treatment of olive oil mill wastewater in a lab-scaled single chamber MEC and the capability of electrical current density generation and hydrogen production were explored, and further experiments were carried out to correctly determine the MEC's optimal condition. To the best of the authors' knowledge, this research is the first report on the successful bioelectrochemical treatment of olive oil mill wastewater with simultaneous hydrogen production in an optimized single chamber MEC.

MATERIALS AND METHODS

All of the chemicals applied in the experiments were of analyti-

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cal grade and obtained from the local market (Merck, Germany). Also, all experiments were performed in batch mode at constant temperature of 37 °C in triplicate.

1. Microbial Inoculum and Wastewater Characteristics

The anaerobic sludge used in this study was acquired from the anaerobic wastewater treatment section of Pegah dairy plant (Tehran, Iran). This sludge had the initial mixed liquor suspended solids (MLSS) of 39 g l^{-1}, which was rather high; hence it was diluted into the MLSS of 2.1, 4.3 and 6.3 g l^{-1} to study the phenol degradation rate. It was observed that the MLSS of 4.3 g l^{-1} had the highest phenol biodegradation rate (when the phenol concentration was 250 mg l^{-1}), so it was chosen for the further experiments in MEC. The acclimation of anaerobic bacteria was completed after 68 days in which the gradual increase of phenol concentration (to 300 mg l^{-1}) inside the serum bottles was performed. The sludge adaptation to phenol is presented in Fig. S1 in the Supplementary Material. Also, the phenol degradation rate for phenol concentrations of 200, 250, and 300 mg l^{-1} was calculated to be about 25.62, 31.5, and 21.43 mg l^{-1} day^{-1}, respectively. Hence, the initial phenol concentration of 250 mg l^{-1}, which had the highest degradation rate, was opted for the further experiments in MEC.

OOMW and the synthetic wastewater (SW) were investigated as substrates in this research. SW was prepared using the following constituents: C_6H_5OH (phenol) (0.25 g l^{-1}), $Na_2HPO_4{\cdot}12H_2O$ (11.546 g l^{-1}), $NaH_2PO_4{\cdot}2H_2O$ (2.769 g l^{-1}), NH_4Cl (0.31 g l^{-1}), KCl (0.13 g l^{-1}), $MgSO_4{\cdot}7H_2O$ (3 mg l^{-1}), $MnSO_4$ (0.43 mg l^{-1}), NaCl (1 mg l^{-1}), $FeSO_4{\cdot}7H_2O$ (0.1 mg l^{-1}), $CaCl_2{\cdot}2H_2O$ (0.1 mg l^{-1}), $ZnSO_4{\cdot}7H_2O$ (0.178 mg l^{-1}), $CuSO_4{\cdot}5H_2O$ (0.01 mg l^{-1}), $AlK(SO_4)_2$ (0.01 mg l^{-1}), H_3BO_3 (0.01 mg l^{-1}).

OOMW composition is extremely variable depending on the type of olive and its ripeness, and also the type of extraction method used in the process [20]. The real OOMW utilized in the experiments was collected from the wastewater unit of olive oil industrial plant (which employed the three-phase extraction method) located in Rudbar, Iran. The OOMW was centrifuged at 8,000 rpm for 15 min, then filtered and autoclaved prior to use. The measurements indicated that OOMW had the COD of 170,000 mg l^{-1} and pH of 5.83, and the content of its polyphenolic compounds equaled 2,400 mg l^{-1}.

2. MEC Setup and Operation

A 500-ml screw cap glass bottle was used as the single chamber MEC reactor. The reactor included pretreated electrodes (electrodes washed with deionized water, dried in the oven and then washed again with HCl (1 molar), deionized water, NaOH (1 molar) and deionized water, respectively) and was connected to a power supply unit (PS-90, MICRO), a multimeter (1860, Pro'sKit) and a 10-ohmic resistor through copper wires. The anode electrode was made of graphite, but the cathode electrode was constructed using stainless steel (mesh size 60). BET analysis showed that the specific surface area of anode and cathode was 13 and 27 m^2 g^{-1}, respectively. Anode electrode was designed in the shape of a plus sign (+) with approximate surface area of 80 cm^2 located exactly in the center of bottle while it was surrounded by cathode (with 3 cm distance from each other), which was cylindrically shaped having a surface area of 160 cm^2. Cell potential was logged by a personal computer every 5 min when different external potentials (0.3, 0.6 and 0.9 V) were applied to the MEC by power supply unit. The low-cost material utilized and application simplicity enhanced this MEC's feasibility for wastewater treatment. Fig. 1 illustrates the setup used in the experiments.

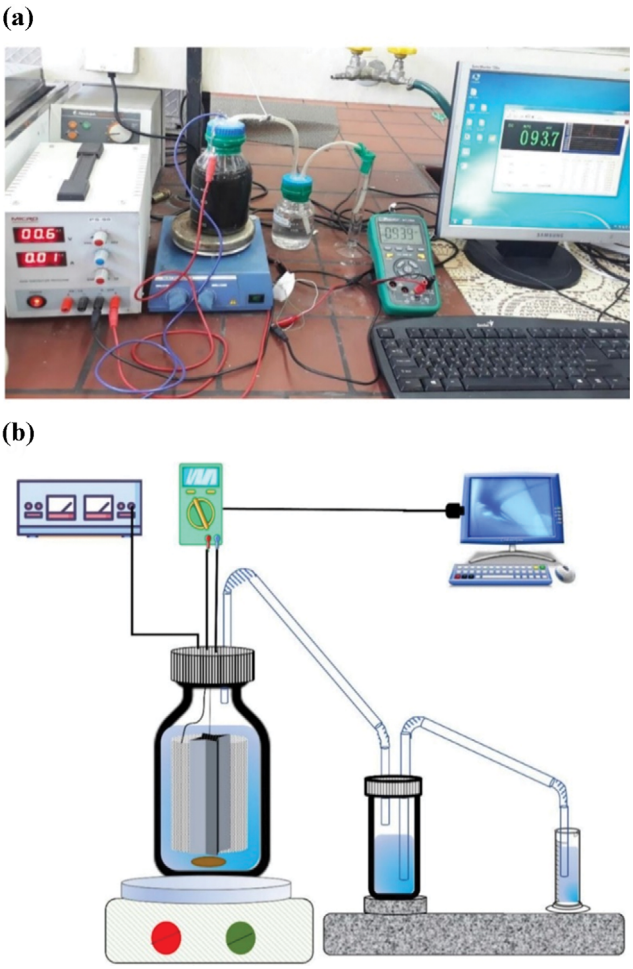

Fig. 1. The MEC's (a) experimental setup and (b) schematic diagram.

Before adding the inoculum and SW, MEC was washed, autoclaved and then purged with N_2; afterwards it was sealed in order to keep the aseptic anaerobic condition. Next, the reactor was batch fed with 500 ml of a mixture of wastewater and anaerobic sludge (MLSS of 4.3 g l^{-1}) while the temperature remained at 37 °C (mesophilic condition) and the rector was constantly agitated at 200 rpm by a hotplate magnetic stirrer. COD and phenol concentration was measured every 24 hours. When the phenol and COD concentration mostly decreased, 200 ml of the anolyte was substituted with fresh wastewater until a sustained condition was obtained. To maintain the anaerobic condition, nitrogen gas was purged into the reactor for 15 min after each feeding or sampling.

3. Analysis and Calculations

MEC performance was constantly monitored by measuring COD and phenol removal, generated current density, hydrogen production rate and the hydrogen recovery.

The MLSS and COD content were analyzed by the standard method [21] and the phenol concentration was estimated by Folin-Ciocalteu method [22] employing a JASCO, V-550 UV/VIS spec-

trophotometer (Tokyo, Japan). Before all measurements, the specimens were centrifuged at 8,000 rpm for 15 min.

Furthermore, BET apparatus (autosorbe1, Quantachrome) was applied to calculate the surface area of electrodes, and current density (current per unit area of anode) was also computed by applying Ohm's law (I=V/R). The volume of produced gas was determined applying the water displacement system as indicated in Fig. 1 and the methane gas was specified via GC (Clarus 680, Perkin Elmer). Hydrogen production rate and the hydrogen recovery were determined with use of the following equations [23]:

$$n_{th}=\frac{b_{H_2/S}v_L\Delta S}{M_S} \quad (1)$$

$$n_{CE}=\frac{\int_{t=0} Idt}{2F} \quad (2)$$

$$r_{CE}=\frac{n_{CE}}{n_{th}}=C_E \quad (3)$$

$$r_{cat}=\frac{n_{H_2}}{n_{CE}} \quad (4)$$

$$Q_{max}=\frac{43.2I_V r_{cat}}{Fc_g(T)} \quad (5)$$

where n_{th} is the number of theoretically produced hydrogen moles based upon the COD decrease, $b_{H2/S}$ shows stoichiometrically produced hydrogen from substrate, V_L indicates the anolyte volume, ΔS is the amount of change in COD, and M_S is the molar weight of substrate. I, n_{CE}, dt and F indicate current, the hydrogen moles which can be recovered based upon the current, time range and Faraday's constant, respectively. r_{CE} and C_E are the Coulombic hydrogen recovery and Coulombic efficiency which are equivalents here. r_{Cat} represents cathodic hydrogen recovery while n_{H2} is the number of recovered hydrogen moles in a batch cycle. Q_{max} presents the maximum rate of hydrogen production, I_V is the volumetric current density during the batch cycle, C_g is the gas molar density, and T is temperature [19,23].

RESULTS AND DISCUSSION

At first, the effect of different applied voltages and cathodes on SW-containing MEC was investigated to find the optimal condition; then the optimum MEC was fed with OOMW, and the OOMW treatment and hydrogen production in MEC were evaluated.

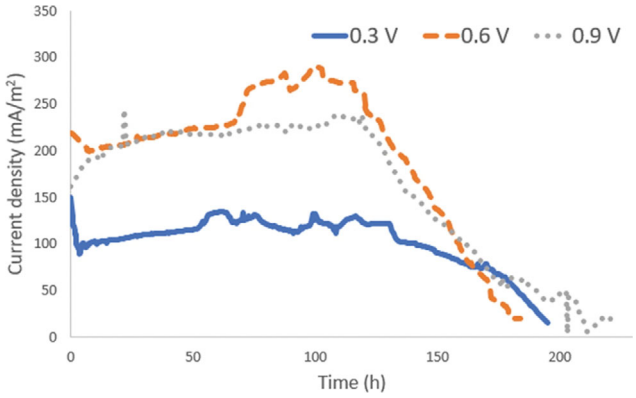

Fig. 2. Temporal distribution of current density at different applied voltages.

1. Effect of Applied Voltage in MEC

Current is produced under closed circuit condition. As shown in Fig. 2, the current evolution over time varied with the various applied voltages (0.3, 0.6 and 0.9 V). The stable peak of current density was observed towards the end, under all applied voltages. By increasing the applied voltage, no specific pattern of stable current densities was observed (it was reported in the literature before [24]), as the stabilized current density under the supplied voltage of 0.6 V was the highest one and the one at 0.3 V was the lowest.

The maximum current densities of 123.5, 274.4, 225.1 mA m^{-2} were obtained at 0.3, 0.6 and 0.9 V, respectively (Fig. 3(a)). Additionally, by measuring the phenol concentration over five days, it was found that the phenol removal was 85% at 0.3 V, then it increased to 96% at 0.6 V and finally slightly decreased to 93% at 0.9 V (Fig. 3(b)). As shown before in Fig. S1 at Supplementary Material, the anaerobic phenol degradation in serum bottle, outside of the MEC, was 80% for 250 mg l^{-1} of phenol during five days; hence, it can be stated that the applied potential had positive effect on phenol degradation in a way that enhanced the removal. By increasing the supplied voltage, phenol removal also increased; however, the removal marginally decreased at 0.9 V which can be related to

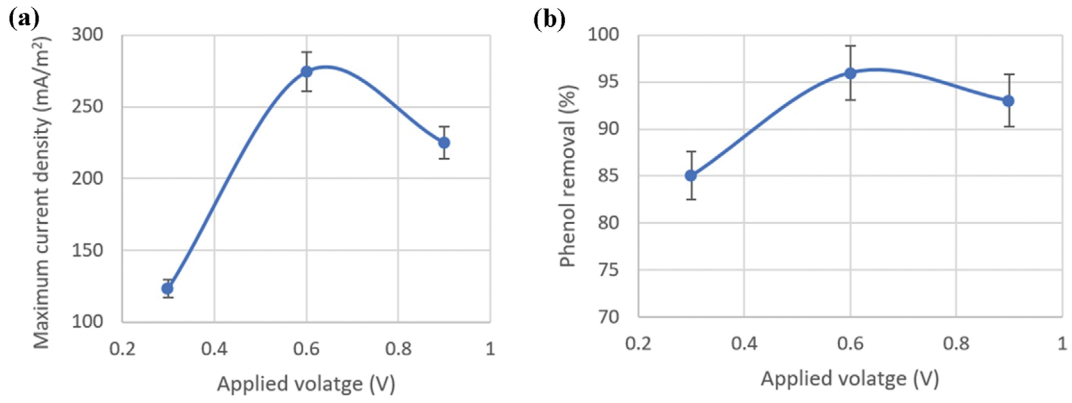

Fig. 3. The change of (a) maximum current density and (b) phenol removal under different applied voltages.

the inhibition effect of anaerobic microbial activities, as reported in the literature [25-27].

The results indicate that the phenol degradation and the maximum produced current were significantly affected by the external potentials. Therefore, since the maximum current density and phenol removal were optimal at 0.6 V, this potential was selected as the proper external voltage to apply in the following experiments.

2. Effect of Cathode Electrodes

To assess the effect of cathodes, two different cathode materials were tested. Stainless steel and graphite are two base cathode materials used in MEC because of their good electrical conductivity, high stability towards chemicals and low price; however, since the stainless steel mesh has high specific surface area [28-30], recently it has become more favorable and been used in numerous studies [29,31-33].

Fig. 4(a) presents the current density of the MECs containing these two cathodes over time. By injecting the fresh SW, the generated current density increased and after some time began to drop, indicating a reduction in organic substrate at the MEC [31]. As seen in Fig. 4(a), the stainless steel cathode produced higher current density in a way that its maximum current density was approximately 100 mA m^{-2} larger than the one for graphite. In addition, according to Cheng and Logan [34] the substance creating the current production's sharpest slope under a certain applied voltage is a good choice for MEC's cathode. Call et al. [29] carried out a comparative study on MECs with different cathode electrodes and concluded that the MEC having stainless steel cathode acted better in producing current density than the one having graphite cathode, and they both generated significantly higher current compared to other applied cathodes. However, they did account for the effect of the cathodes on the biodegradation of contaminant.

Phenol concentration and COD inside the MECs with the two aforementioned cathodes at the external potential of 0.6 V is presented in Fig. 4(b) and (c), respectively. The phenol degradation rate was higher using the stainless steel; i.e., phenol was eliminated completely in 144 hours for stainless steel cathode, while this happened over 168 hours of operation for graphite cathode. On the other hand, the maximum COD removal of 73% was obtained for MEC with stainless steel, which was 12% higher than the one for graphite-cathode MEC.

Overall, the better performance belonged to the stainless steel as a suitable cathode for MEC; therefore, the stainless steel-equipped MEC was chosen for the subsequent experiments. However, for future studies it is recommended to coat the electrode with catalysts to decrease the needed activation energy for electrode reactions and, thus, increase the produced current density and COD removal. Also, the type of functional bacterial group which will stick to the given electrode surface in the MEC affects the composition of produced gases [35,36] and electron recovery on cathode [37].

3. Olive Oil Mill Wastewater Treatment

OOMW was treated in an MEC equipped with stainless steel

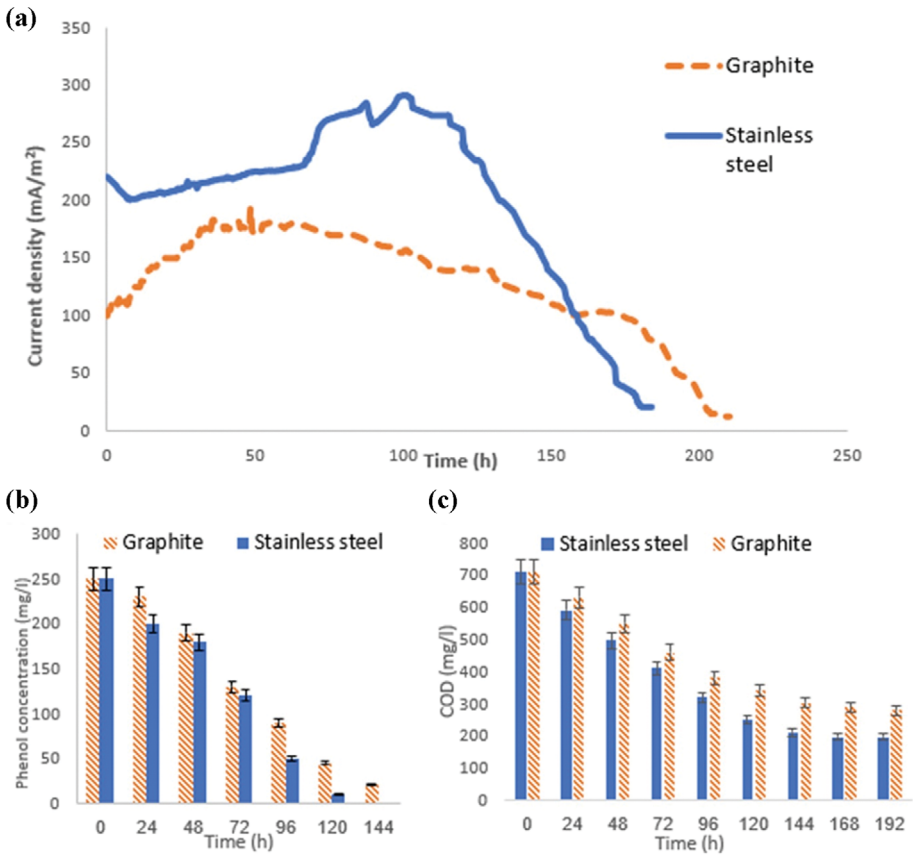

Fig. 4. (a) Current density, (b) phenol concentration and (c) COD for various cathodes.

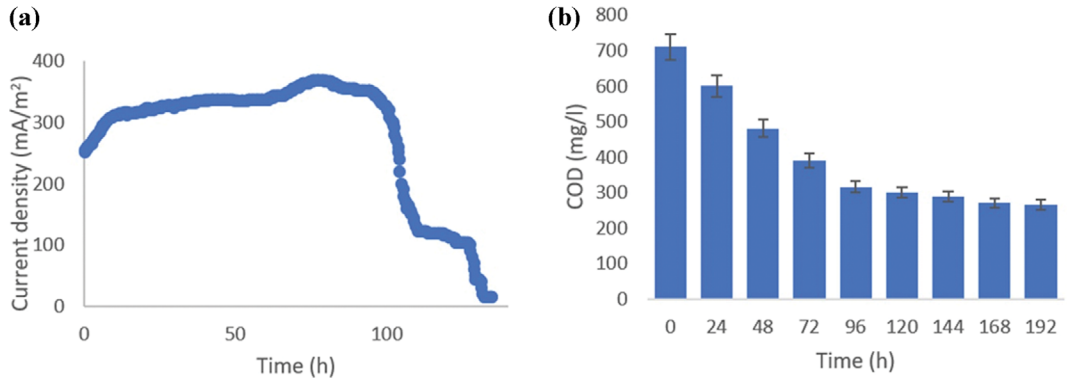

Fig. 5. (a) Produced current density and (b) COD over time for stainless steel-cathode MEC treating OOMW at applied voltage of 0.6 V.

Table 1. Hydrogen production and other cell parameters for SW and OOMW treatment in MEC at 0.6 V

Wastewater	n_{th} (mole)	n_{CE} (mole)	C_E or r_{CE} (%)	r_{cat} (%)	Q_{max} (m^3 H_2 m^{-3}·d^{-1})	Q'_{max} (g H_2 l^{-1}·d^{-1})
SW	0.037	0.0055	15	85	0.045	0.00405
OOMW	0.0317	0.0073	23	81	0.053	0.00477

cathode at 0.6 V. Although this wastewater can have negative influence on the optimal performance of the system due to its toxic and inhibitory effect on microbial activities, it also contains many nutritious organic contents desirable for microorganisms and consequently good for MEC's performance [38]. The anaerobic sludge employed in this study had a great ability to treat this wastewater as it was acclimated to phenol and other intermediate reactants produced during phenol biodegradation pathway in the MEC.

COD removal efficiency signifies how much MEC has been successful in the wastewater treatment process. The wastewater's high COD and phenolic compounds can poison the bacteria; therefore, OOMW was diluted to the COD of 715 mg l^{-1} and then added to MEC. After 72 hours, the maximum produced current density of 362 mA m^{-2} was observed (Fig. 5(a)), which was 32% higher than the one generated by SW in MEC. The change in COD for 192 hours is indicated in Fig. 5(b), showing the COD removal of 62%. It can be seen that COD was reduced dramatically till 96 hours and after that it decreased slightly in a way that after 168 hours it remained roughly the same. It goes without saying that the COD reduction strongly depended on wastewater residence time in MEC.

4. Hydrogen Production

The measurements were taken after seven days and the gas production rate was 5.11 ml d^{-1} and 5.72 ml d^{-1} for SW and OOMW, respectively. Inorganic components and poisonous elements present in the wastewater can inhibit the microorganisms and cause low gas production [12].

The maximum hydrogen production, cathodic hydrogen recovery and coulombic efficiency (Coulombic hydrogen recovery) for MECs treating SW and OOMW at 0.6 V are given in Table 1. The coulombic efficiency of OOMW-containing MEC was 8% higher than the one of SW-fed MEC; however, both coulombic efficiencies were low, which may indicate probable oxygen diffusion, high internal resistance and electrode overpotential.

The cathodic hydrogen recovery for SW and OOMW-fed MECs was calculated as 85% and 81%, respectively. Cathodic hydrogen recovery can be affected by a microorganism's attributes and the changed surface area of cathode (due to oxidation) [39]. Besides, a slightly higher hydrogen production rate was observed for OOMW when compared to SW. As the hydrogen production rates were relatively low in this research, the hydrogen loss via the reactor and tubes became more considerable. Producing hydrogen through bioelectrochemical systems introduces an instantaneous way to create the sustainable, renewable and environmental-friendly energy which can be used for transportation [19].

5. Comparison of the Results between the Present Work and Previously Reported Studies

Bioelectrochemical systems are a new method for power production, contaminant biodegradation and producing useful products (such as methane and hydrogen gas). In this section the obtained results of this study were compared to others in terms of the three aforementioned aspects.

5-1. Biohydrogen Production

Coulombic efficiency is one of the imperative parameters indicating the MEC's performance since it denotes efficiency as of the supplied energy and the acquired wastewater treatment. A wide range of Coulombic efficiencies is documented in the studies (Table 2).

Hydrogen consumption by methanogens is one of the main problems in producing hydrogen gas through MEC [40,41]. Cusick et al. [42] produced a huge amount of methane by applying a pilot-scale (1000 l) MEC. They implied that since they did not isolate the generated hydrogen gas, a large quantity of methane was produced. Montpart et al. [43] used different substrates as carbon source in MEC and reported that they could produce a large amount of methane and almost no hydrogen due to the low rate of hydrogen production and hence its transformation to methane. In another research, Zamalloa et al. [44] produced methane in a lab-scaled MEC (with volume of 20 l) in a way that its quantity was 400% more than that of anaerobic reactor; and they stated that since they could not separate and restore hydrogen gas during the process, the produced methane gas increased. Furthermore, the same

Table 2. Summary of the produced biohydrogen in different works

MEC reactor	Substrate	Applied voltage (V)	Coulombic efficiency (%)	Hydrogen production rate (m^3 H_2 m^{-3}·d^{-1})	Reference
Single chamber	Dewatered sludge	0.9	78.89	0.038	[50]
Double chamber	Urban wastewater	1.5	28	0.032	[40]
Single chamber	Dairy wastewater	0.7	24	0.2	[51]
Double chamber	Synthetic wastewater	1.2	21	0.22	[52]
Double chamber	Vinasse residue	0.2	74.1	0.066	[53]
Single chamber	Urban wastewater	Variable	25-75	0.05	[54]
Double chamber	Domestic wastewater	0.6	55	0.015	[47]
Single chamber	Synthetic wastewater (phenol)	0.6	15	0.045	Present study
Single chamber	Olive oil mill wastewater	0.6	23	0.053	Present study

Table 3. Summary of the current production in different works

Reactor type	Anode surface area (cm^2)	Volume (ml)	Produced current density (mA m^{-3})	Reference
MEC	210	250	2,000	[55]
MEC	19,680	120,000	135	[47]
MFC	65	210	928.5	[56]
MEC	2,200	28	1,150	[57]
MFC	180	550	663	[32,33]
MEC	80	500	4,390	Present study
MEC	80	500	5,792	Present study

Table 4. Summary of the substrate's improved biodegradation rate at bioelectrochemical systems in different works

Reactor type	Substrate	Initial concentration (mg l^{-1})	Biodegradation rate improvement compared to anaerobic digestion (%)	Reference
MFC	Phenol	400	15	[58]
MEC	VFA	200-1,200	27	[59]
MEC	Waste activated sludge	8,000 (COD)	5-10	[60]
MEC	Black water	5,000-7,000 (COD)	<5	[44]
MEC	Phenol	250	16	Present study
MEC	Olive oil mill wastewater	715 (COD)	10	Present study

increase in methane production by MEC compared to their equivalent anaerobic digestion process was reported by two studies [45,46], but the difference was that the larger reactor (9.5 l) had much more methane gas than the smaller one (0.5 l). Considering these researches, it can be presumed that small MEC reactors are more capable of producing hydrogen gas with high purity and high-volume reactors are more suitable for mass production of methane gas. Concerning this matter, a double chamber MEC was employed by Heidrich et al. [47] to treat domestic wastewater, and a low rate of produced hydrogen with high purity (98%) was obtained. The hydrogen purity was absolutely noticeable in comparison with the purity achieved in a single chamber MEC (<87%), attributable to unfavorable anode reaction (hydrogen recycling) where homoacetogenic microbes consume hydrogen to generate acetate [42,48, 49]. Other studies concerning hydrogen production are listed in Table 2.

5-2. Electrical Current Production

The current densities produced in different bioelectrochemical systems are presented in Table 3. It can be seen that the current generation in this study was rather negligible; however, it can be improved by using suitable microorganisms and electrodes with higher specific surface areas.

5-3. Wastewater Treatment

In Table 4, several studies employing bioelectrochemical reactors as a wastewater treatment system are recorded and their contaminant removal rate is compared with conventional anaerobic digestion. These results show that bioelectrochemical systems sometimes can compete with other anaerobic wastewater treatment systems in terms of COD removal rate.

CONCLUSION

The optimal single chamber MEC with anaerobic sludge developed in this research performed successfully for olive oil mill wastewater treatment as well as hydrogen production. Thus, the optimal MEC condition was characterized by synthetic wastewater, differ-

ent applied voltages and different cathodes. Best applied voltage was 0.6 V in this study and stainless steel cathode had better outcome than graphite cathode, which indicates that a large specific area of the anode could lead to relatively higher current production and substrate degradation. Moreover, higher current production, coulombic efficiency and hydrogen production were obtained for OOMW in comparison with SW. The attained hydrogen gas from the MEC confirmed that smaller MEC reactors are more suitable for producing hydrogen gas than methane. An increase in the obtained wastewater biodegradation rate in the MEC when compared to the conventional anaerobic digestion suggests that the bioelectrochemical process can be a new method to improve biodegradation of recalcitrant contaminants, and sometimes bioelectrochemical systems can compete with other anaerobic wastewater treatment systems. Isolation of the generated hydrogen is recommended to prevent the hydrogen transformation to methane and hence produce higher quantity of hydrogen gas. Also, applying different catalyst coating cathode to reduce the activation energy of electrode reactions and, thus, intensify the current density can be the subject of future studies.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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