



## Performance of pig slurry based microbial fuel cell during energy recovery and waste treatment

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Received 8 April 2016; Accepted 14 August 2016

### ABSTRACT

The performance of two single-chamber air cathode microbial fuel cells (MFCs) fed with pig slurry (MFC1) and synthetic wastewater (MFC2) were studied for energy recovery and waste treatment by applying three different flow recirculation (mixing intensities). The flow recirculation in the MFCs was an important factor on the performance of the MFCs. During pig slurry treatment, the maximum power density was 27.7 mW m<sup>-2</sup> without flow recirculation. The highest removal of chemical oxygen demand (COD) (89.8%), ammoniacal nitrogen (NH<sub>4</sub>-N) (78.2%), total phosphorus (TP) (36.3%), and total suspended solids (TSS) (95%) were achieved under 74 mL min<sup>-1</sup> of flow recirculation. In order to compare the electricity production in the MFC fed with pig slurry, one MFC was fed with synthetic wastewater. Lower power densities were obtained using synthetic wastewater (0.5–3.8 mW m<sup>-2</sup>). The maximum removal of COD, NH<sub>4</sub>-N, TP, and TSS during synthetic wastewater treatment was obtained applying at a flow recirculation of 152 mL min<sup>-1</sup>. The SEM image and EDX spectrum in cation-exchange membrane from MFC1, showed the presence of struvite on membrane surface. In MFC2, the calcium (Ca) and phosphorus (P) ions in form of calcium phosphate salt were detected on membrane surface. The presence of Ca, magnesium (Mg), and P ions precipitated on membrane surface was reduced by applying the highest flow recirculation in both MFCs.

*Keywords:* Air cathode microbial fuel cells; Pig slurry; Bioelectricity; Membrane fouling; Struvite

### 1. Introduction

Each year, approximately 1.3 billion tons of food and agricultural waste are generated worldwide and must be treated in order to reduce the environmental impact caused by these wastes [1]. The problem of high strength wastewater – which involves energy issues and has to do with global climate change – has led to developing new sustainable treatment technologies in order to obtain energy sources from

waste (wastewaters, sewage sludge, and biomass) and simultaneously reduce the pollution generated by these products. Likewise, the high consumption of electrical energy at the treatment plants' sewage was an invitation to develop alternative treatment technologies.

Food and animal waste are high-strength wastewaters which contain great amounts of organic matter, solids, oils and greases, and inorganic components (nitrogen and phosphorus). These wastewaters are released from food and agricultural industries [2,3]. In order to reduce these pollutants – both anaerobic and aerobic or anaerobic/aerobic – sequential biological treatment processes are applied [4,5]. However,

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the aerobic processes require higher amounts of aeration rate impacting on the energy consumption of the wastewater treatment plant. According to Chan et al. [6], Pant et al. [7] and Pham et al. [8], the anaerobic treatment is effective for high strength wastewater and generates recovery energy in the form of methane or hydrogen. The disadvantage of the anaerobic technology is the control of the reactor (pH reduction, volatile fatty acid, toxic and high ammonia concentrations).

In the context of high-strength, pig slurry from livestock and poultry breeding is one of the most abundant sources of organic matter, solids, oils and greases, nitrogen and phosphorus, which are released mostly to the environment without receiving a prior treatment [9,10]. Wastewater technologies have been used for pig wastewater treatment (anaerobic digesters, anaerobic and aerobic sequential batch reactor, biofilters, anaerobic and aerobic lagoons, advanced oxidation processes) [10–21].

Recently, it has been shown that the microbial fuel cells (MFCs) can be used for bioenergy production (electricity, methane, and hydrogen) from municipal and high-strength wastewaters [2,11,20,22–24]. The bio-electrochemical systems are capable of generating electricity from the oxidation of organic matter contained in food and agricultural wastewater (slaughterhouses, brewery, dairy, molasses, and palm) [2,3,25]. However, few researches have reported high-strength pig wastewater from poultry breeding farms applying air cathode MFC [11,20,26]. Pig slurry has not been studied in the MFC yet. It was more specific about of pig slurry. The term “pig slurry” is referred to a mixture of urine, excrement, and water, and two phases can be distinguished: the liquid one, that consist of different nitrogen species, and the solid one, that consists of phosphorus and organic matter. In this study, it was tested the feasibility of using a single-chamber air cathode MFC, operating in batch mode to produce electricity using pig slurry waste (PSW) and achieving a simultaneous removal of contaminants applying different mixing intensities employing flow recirculation inside the MFC.

## 2. Materials and methods

### 2.1. MFCs configuration

Two single-chamber air cathode MFCs at a volume of 183 mL were employed. A cell (MFC1) was fed with PSW and another one (MFC2) with synthetic wastewater (SWW). Carbon cloth (superficial area of 0.0016 m<sup>2</sup>) was used as anode. The cathode consisted of two layers in the following order: cation-exchange membrane (CEM), and carbon fiber. The carbon fiber was impregnated with a PbO<sub>2</sub> catalyst layer (0.5 mg cm<sup>-2</sup>). The distance between anode and cathode was 10.1 cm. Each MFC unit was worked under closed circuit mode at a resistor of 1,200 Ω. A peristaltic pump dual head was used to ensure a same flow recirculation in each MFC.

### 2.2. Wastewater samples

The MFC1 was fed with PSW from the maternity area of a pig farm located in Jojutla, Morelos, Mexico. The MFC2 was fed SWW which contained sucrose (4 g L<sup>-1</sup>), NH<sub>4</sub>Cl (0.2 g L<sup>-1</sup>), CaCl<sub>2</sub> (0.19 g L<sup>-1</sup>), KCl (0.33 g L<sup>-1</sup>), NaCl (0.3 g L<sup>-1</sup>), K<sub>2</sub>HPO<sub>4</sub>

(1.26 g L<sup>-1</sup>), KH<sub>2</sub>PO<sub>4</sub> (0.42 g L<sup>-1</sup>), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.68 mg L<sup>-1</sup>), ZnCl<sub>2</sub> (1.25 mg L<sup>-1</sup>), MnCl<sub>2</sub>·4H<sub>2</sub>O (12.5 mg L<sup>-1</sup>), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>6</sub>O<sub>24</sub>·4H<sub>2</sub>O (0.07 g L<sup>-1</sup>), CoCl<sub>2</sub>·6H<sub>2</sub>O (3.75 mg L<sup>-1</sup>), NiCl<sub>2</sub>·6H<sub>2</sub>O (2.5 mg L<sup>-1</sup>), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.5 g L<sup>-1</sup>) y H<sub>3</sub>BO<sub>3</sub> (1.25 mg L<sup>-1</sup>). The chemical oxygen demand (COD) of SWW was similar to PSW in order to determine the influence of other contaminants, such as the ammoniacal nitrogen (NH<sub>4</sub>-N), and total suspended solids (TSS) on the electricity production from MFCs.

### 2.3. Inoculation

The MFCs were inoculated with anaerobic granular sludge from a UASB reactor at the paper industry wastewater. Granular sludge was dissolved and held in suspension in SWW and pig slurry and incubated for a period of 67 h at a temperature of 30°C, before being inoculated into the MFCs. The amount of TSS inoculated into each MFC was 59,750 mg L<sup>-1</sup>.

### 2.4. MFCs operational condition

The MFCs were operated in batch mode. Both MFCs worked simultaneously mixing three conditions (variation in the flow recirculation). In the first operating condition (R1), the MFCs worked statically (without recirculation). In the second condition, the recirculation (R2), the flow was 74 mL min<sup>-1</sup> and in the third one (R3), the flow recirculation was 152 mL min<sup>-1</sup>. The operating cycle of the MFCs was determined by the decrease in voltage over time (approximately 80% from the maximum voltage generated in each MFC) for each operating condition. The pig slurry and SWW were replaced completely at the end of each fed-batch cycle of the MFCs. At the end of each operating condition, the membranes were removed and replaced with virgin membranes to begin the following operational condition.

### 2.5. Calculations and analysis

The performance of MFCs was evaluated by voltage ( $V$ ), electric current ( $I = V/R_{ext}$ ), electric power ( $P = I \times V$ ), power density ( $P/Area_{electrode}$ ), coulombic efficiency (CE), theoretical and experimental energy production ( $W$ ).

CE is defined as the ratio between the number of coulombs actually transferred to the anode from the substrate and the maximum number of coulombs transferred, if the entire substrate was capable of producing current. According to Pasupuleti et al. [27], and Logan [28], the EC for MFC operated in batch mode was given by Eq. (1):

$$CE = \frac{32 \int_0^t I(t) dt}{F b v \Delta COD} \quad (1)$$

where  $I(t)dt$  is the total coulombs transferred in MFC,  $t$  is the operation cycle of MFC (h),  $F$  is the Faraday's constant (96485 C mol<sup>-1</sup>),  $b$  is the number of electrons exchanged per mol of oxygen,  $v$  is the volume of MFC (L) and,  $\Delta COD$  is the COD<sub>initial</sub> - COD<sub>final</sub> (mg L<sup>-1</sup>). The calculation of CE was performed by the method of trapezoids ( $n = 16$ ).

The total generation of experimental energy ( $W_{experimental}$ ) was determined during the operating cycle of the MFCs

and it represented the energy that it generated through the removal of COD, involving internal resistance of each MFC in each operating condition (Eq. (2)).

$$W = \int_0^t \frac{V^2}{R_{\text{ext}}} dt = \frac{R_{\text{ext}} + R_{\text{int}}}{R_{\text{ext}}} \quad (2)$$

where  $W_{\text{experimental}}$  is the experimental energy (joules),  $t$  is the operation cycle of MFC (h),  $V$  is the voltage generated in MFC (mV),  $R_{\text{ext}}$  is the external resistor (1,200  $\Omega$ ) and  $R_{\text{int}}$  is the internal resistance ( $\Omega$ ).

The overall performance of the MFCs were evaluated in terms of COD, TSS,  $\text{NH}_4^+\text{-N}$ , total phosphorus (TP) and nitrates ( $\text{NO}_3\text{-N}$ ) according to standard methods [29].

### 2.6. Scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX) analysis for observation of the structure bioanode and fouling membranes in MFCs

For SEM-EDX analysis, part of the membranes and anodes were cut into pieces (0.25  $\text{cm}^2$ ) and fixed in 5% glutaraldehyde and 5% dehydrated in a solution of ethanol-deionized water. Anodes and membranes samples were carefully rinsed with monosodium phosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ) and disodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) at pH 7. After, were subject to dehydration using ethanol series 50%, 60%, 70%, 80%, and 100%; 30 min for each concentration. Before the observation on SEM-EDX, the samples were coated with gold-palladium for 30 min under vacuum on a Sputter Coater SC7620. The morphology and elemental components of anodes and CEMs were analyzed by microscope SEM LEO 1450VP equipped with ICA EDX detector.

## 3. Results and discussion

### 3.1. Physico-chemical characterization of PSW and SWW

The PSW showed high concentrations of organic matter, solids, phosphorus, and ammoniacal nitrogen. The COD of the pig slurry was 4,237  $\text{mg L}^{-1}$ . The  $\text{NH}_4\text{-N}$  was detected in high concentrations (790  $\text{mg L}^{-1}$ ). This inorganic compound may have a positive influence on the generation of electricity, according to the process of nitrification-denitrification and anammox (anaerobic ammonium oxidation), which may occur within the MFC and can release protons ( $\text{H}^+$ ) into the MFC. These can be used to generate a potential difference increasing the flow of electrons in the MFC [30]. The nitrate concentration was 5  $\text{mg L}^{-1}$ . TSS was found in 2,502  $\text{mg L}^{-1}$ , pH 7.7 and a conductivity of 7.9  $\text{mS cm}^{-1}$ . The TP was 73  $\text{mg L}^{-1}$ . The SSW used had a COD of 4,197  $\text{mg L}^{-1}$ ,  $\text{NH}_4\text{-N}$  of 51  $\text{mg L}^{-1}$ , TP of 8  $\text{mg L}^{-1}$ , pH 7 and a conductivity of 0.8  $\text{mS cm}^{-1}$ .

### 3.2. Power generation profile using MFCs under three regimes of flow recirculation

Before operating the MFCs under different mixing conditions, the MFCs were previously inoculated and acclimated to pig slurry and SWW for 50 days, in order to form the biofilm on the anode and generate a stabilization of voltage at open circuit. During the acclimatization stage, the voltage at open circuit was 765 mV and 543 mV for MFC1 and MFC2,

respectively. Fig. 1 shows the MFC1 performance under the three operating conditions. When the pig slurry remained without recirculation, the maximum voltage of 234 mV was achieved (power density of 27.5  $\text{mW m}^{-2}$ ). The voltage for this condition began to decline after 168 h of operation of the MFC. The operation cycle of MFC1 with R1 was 218 h. For R2, the maximum voltage was 221 mV with power density of 24.5  $\text{mW m}^{-2}$ . The operating cycle was 94 h. For R3, the maximum voltage was 223 mV and the operation cycle was 74 h. The power density under this condition was 24.8  $\text{mW m}^{-2}$ . It was observed that the power densities of MFC1 under three regimens of recirculation were not significantly affected by the recirculation rate. However, a significant difference was observed in the cycles of operation. When increasing the flow of recirculation, the operation cycles of MFC1 were reduced. This behavior indicates that the biofilm adhered onto the carbon cloth and the pig slurry in contact with mixing, the mass transfer is further allowed the organic matter to be degraded faster, thus affecting simultaneously the time of electricity production. Conversely, when the MFC1 was operated without a flow recirculation, the microorganisms are in less contact with the substrate generating a lower mass transfer, which means that the organic matter is degraded more slowly, stimulating one production of electricity longer.

The MFC2 generated a lower voltage compared with MFC1. The maximum voltage obtained in the MFC2 was 83 mV (power density of 3.5  $\text{mW m}^{-2}$ ) for a flow recirculation of 0  $\text{mL min}^{-1}$  (R1) (Fig. 1). With R3, electricity production was smaller compared with R2 and R1. The operating cycle

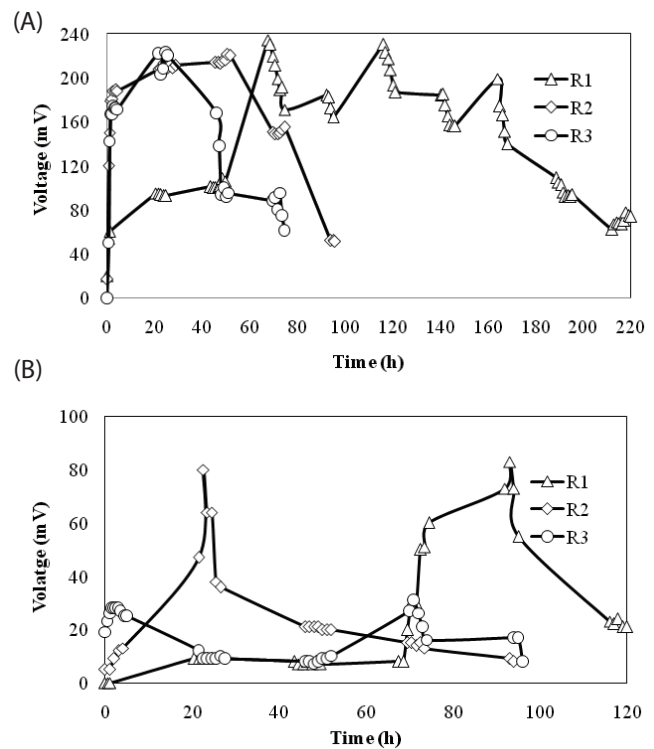


Fig. 1. Profiles of voltage during performance of MFC1 (A) and MFC2 (B) under different flows recirculation (R1 = without mixing; R2 = 74  $\text{mL min}^{-1}$ ; R3 = 152  $\text{mL min}^{-1}$ ).

for R1, R2, and R3 was 119, 94, and 96 h, respectively. The difference between the voltages generated in the MFC1 and the MFC2 was influenced by the concentration of ammonia nitrogen, which serves as a type of substrate or co-substrate to produce electricity. Furthermore, the MFC1 was favored by high conductivity in PSW, which facilitated the flow of electrons and protons in the aqueous phase compared with the MFC2. In the MFC2, the synthetic solution generated high internal resistance and low power densities.

### 3.3. Treatment of PSW and SWW in MFCs

Table 1 shows the removals of COD, TSS,  $\text{NH}_4\text{-N}$ , and TP obtained in the MFC1 and the MFC2 under three operating conditions. For the MFC1's maximum removal of contaminants, it was applied a speed of recirculation of  $74 \text{ mL min}^{-1}$  (R2). The COD values decreased up to  $432.2 \text{ mg L}^{-1}$  (89.8% removal), ammoniacal nitrogen concentration decreased from  $790$  to  $172.2 \text{ mg L}^{-1}$  (78.2% removal) and the TP removal was 36.3%. Certain amount of phosphorus removed by the MFC1 and the MFC2 was precipitated in the CEM, which are shown in the analysis by SEM-EDX. Removals between 14% and 82% of TP were obtained in a single-chamber microbial electrolysis cell and air cathode MFC [11,26,31]. Min et al. [20] obtained removals of COD and ammonia nitrogen of 86% and 83%, respectively. However, these researchers conducted a dilution of swine wastewater ( $1_{\text{pig wastewater}}/10_{\text{fresh water}}$ ). Ichihashi and Hirooka [11] and Ichihashi et al. [26] obtained COD removals between 76% and 91% in an air-cathode MFC fed-batch mode with an operating cycle of 76 days. The TSS removal in MFC1 was as high as 95% ( $125 \text{ mg TSS L}^{-1}$ ). High removals of TSS are related on one side to the precipitation of salts on the surface of the membrane and on the other to the particulate solids that adhered to the membrane surfaces. This effect generated possibly that voltages in both MFCs were not stable due to the formation of a barrier that prevent the protons transfer through of the membranes. For the MFC2, the maximum removal of COD (73.1%)  $\text{NH}_4\text{-N}$  (71.2%), and TP (25.5%) was reached by applying a recirculation of  $152 \text{ mL min}^{-1}$  (R3). As the recirculation rate was increased, the removal of contaminants increased because there was a greater mass transfer and microorganisms were in closer contact with the substrate. Although the MFC1 with R2 and R3 had the best removal of contaminants, the one without recirculation condition also generated a good removal of COD,  $\text{NH}_4\text{-N}$  and TP. Yokoyama et al. [32] reported that

the removal efficiency of a two-chamber MFC fed with cow waste slurry was 85% of biochemical oxygen demand, 84% of nitrogen, 70% of TP, and 91% of potassium.

It has been that the nitrogen may cause problems in anaerobic digestion since the ammonium in high concentrations may lead to the inhibition of the biological process. However, in this study was not observed an inhibitory effect of the biological processes. The two MFCs generated high  $\text{NH}_4\text{-N}$  removals, which can be explained by two reasons: 1 Partial nitrification within the anode chamber caused by oxygen diffusion through the cathode generating nitrates and serving as an electron acceptor for the denitrification and 2 Due to anammox process. The concentration of nitrites and nitrates detected in the MFC1 was  $13 \text{ mg L}^{-1}$  and  $34 \text{ mg L}^{-1}$ , respectively. In the MFC2, the nitrites concentrations were  $2 \text{ mg L}^{-1}$  and nitrates were  $7 \text{ mg L}^{-1}$ . Both nitrites and nitrates served as final electron acceptor in denitrification and anammox process. According to Min et al. [20], Zhang and He [30], Yan et al. [33] and Lui and Logan [34] one nitrification process occurs inside an anodic camera near an air-cathode. In this study, the cathodes were not coated with PTFE layer, generating the diffusion of atmospheric oxygen through of cathode.

### 3.4. Polarization curves and internal resistance

The polarization curves were obtained by changing the external resistance using a resistor portable box/load bank (Fig. 2). For MFC1, the power density for R1 was  $27.7 \text{ mW m}^{-2}$  with a current density of  $118 \text{ mA m}^{-2}$ . The power density for R2 was  $24 \text{ mW m}^{-2}$  for a current density of  $109 \text{ mA m}^{-2}$ . R3, the maximum power density obtained was of  $25 \text{ mW m}^{-2}$  (current density of  $149 \text{ mA m}^{-2}$ ). The maximum value of power density for the MFC2 was  $3.8 \text{ mW m}^{-2}$  with a current density of  $53.4 \text{ mA m}^{-2}$  when the MFC was operated without recirculation. For R2, the power density was  $3.5 \text{ mW m}^{-2}$  with a current density of  $42.1 \text{ mA m}^{-2}$ . The power density obtained for R3 was  $0.5 \text{ mW m}^{-2}$ , with a power density of  $10 \text{ mA m}^{-2}$ . Power densities obtained in the MFC1 were low, compared with other studies where power densities were reached up to  $261 \text{ mW m}^{-2}$  using swine wastewater [26]. The low densities of this study are linked to the presence of high concentrations of TSS and to the fact that about 50% of the COD of pig wastewater corresponded to particulate material, which limited the substrate diffusion through cell membranes of bacteria electricity (electrogenic bacteria),

Table 1  
Pollutants removal and maximum power obtained from MFC1 and MFC2 during pig slurry and synthetic wastewater treatment

Flow recirculation conditions	MFC1					MFC2					
	COD removal (%)	$\text{NH}_4\text{-N}$ removal (%)	TP removal (%)	TSS removal (%)	Voltage (mV)	Operation cycle (h)	COD removal (%)	$\text{NH}_4\text{-N}$ removal (%)	TP removal (%)	Voltage (mV)	Operation cycle (h)
Without mixing	73.1	40.8	22.1	78.8	234	218	41.4	33.5	18	83	118
R2	89.8	78.2	36.3	95.0	221	94	54.6	65.4	19.3	80	94
R3	89.8	67.4	34.0	95.0	223	74	73.1	71.2	25.5	31	96

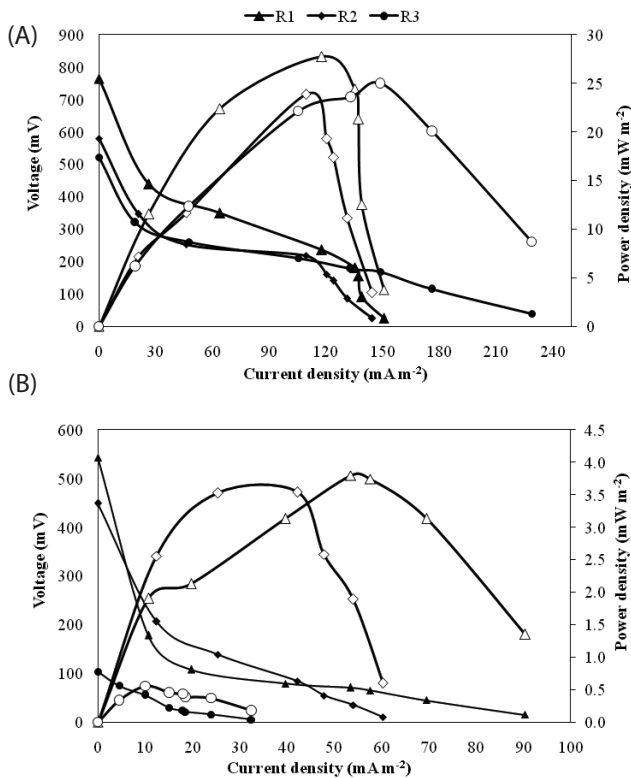


Fig. 2. Polarization curves of MFCs under different flow recirculation (R1 = without mixing; R2 = 74 mL min<sup>-1</sup>; R3 = 152 mL min<sup>-1</sup>): (A) pig wastewater; (B) synthetic wastewater.

generating low power densities. The power densities reported via MFCs with the others manure from animal cattle, cow and dairy are diverse. Cattle manure was examined in two membrane-less MFC configurations. The power density generated was 36.6–67 mW m<sup>-2</sup> [35]. Wang et al. [36] investigated the production of electricity in a single-chamber air-cathode MFC fed with cow manure which showed that a higher moisture content (80%) was more suitable for current generation (349 mW m<sup>-2</sup>) compared with moisture content at 60% (12 mW m<sup>-2</sup>). In other study, the maximum power density in a two-chamber MFC was 0.34 mW m<sup>-2</sup> fed with cow waste slurry. This low current generation resulted from the presence of high inorganic matter, cellulose, and lignin concentrations in manure, according to Yokoyama et al. [36].

The internal resistance was calculated by the method of the slope of the voltage polarization curves ( $R_{int} = m/A_{electrode}$ ). In the MFC1, the calculated internal resistance was 2340, 1742, and 1,026  $\Omega$  for R1, R2 and R3, respectively. For MFC2, the internal resistance for R1 was 2,500, 3,777  $\Omega$  for R2 and R3 of 1,841  $\Omega$ . It was determined that with a higher flow recirculations applied in both MFCs, internal resistances were lower indicating that the higher turbulence inside the MFCs, the internal resistances are reduced.

### 3.5. Coulombic efficiencies and experimental energies from MFCs

To determine the CE, experimental energy integration was performed using the method of the trapezoids. From the coulombs generated, which were obtained by integrating

Table 2  
Coulombic efficiencies and energy losses obtained from MFC 1 and MFC 2

	Flow recirculation conditions (mL min <sup>-1</sup> )	Coulombic efficiency (%)	Experimental energy (joules)	Operational cycle (h)
MFC1	Without mixing (R1)	33.3	374.2	218
	74 (R2)	12.2	175.4	94
	152 (R3)	1.4	34.3	74.5
MFC2	Without mixing (R1)	38.1	60	119
	74 (R2)	1.4	4.4	94
	152 (R3)	4.2	3.2	96

the current over time the initial and final values of COD, the internal resistance and external resistor, the coulombic efficiencies, and experimental energies in the MFCs were obtained. Table 2 shows the coulombic efficiencies and experimental energies generated during pig slurry and SWW in MFCs. For the MFC1, the greater CE was 33.3% with an experimental energy of 374.2 joules, which were obtained without recirculation condition. In the MFC2, the greater EC and experimental energy were also without recirculation conditions with values of 38.1% and 60 joules, respectively. The maximum power densities generated in the MFC1 and the MFC2 correspond to high values of ECs. In studies realized by Ichihashi and Hirooka [11] for phosphorus removal and recovery struvite during porcine wastewater in MFC, the EC obtained were between 37% and 47%. In other studies, the EC was 30%–38% in the MFC through swine wastewater [26]. The MFC-cycle time was a relevant factor during the operation of the MFCs because, at high cycles of operation on the MFC, the energies increased.

### 3.6. Observation and analysis of the elemental chemistry bioanodes and membranes of MFCs by SEM-EDX

The bioanodes of MFCs were extracted after the experimentation and cut into small pieces for analysis by SEM. The membrane of each MFC was extracted after each operating condition and was observed and analyzed by SEM-EDX to determine the membrane fouling. Biofilms formed on the carbon cloth of the MFCs were good structure and morphology (Fig. 3). For MFC1 (Fig. 3(A)), several organic compounds were observed due to the physico-chemical composition of PSW water. In the anodes of the MFCs, microorganisms of different shapes and sizes (bacilli which have rod-shaped, coconuts spherical form spores and extracellular polymeric substances) were found.

In Figs. 4 and 5, it can be observed the surface morphology of MFCs membranes after being used in each operating condition. On the surface of the CEMs, it was formed a thin and uniform film of solids composed mainly by inorganic and organic components (Figs. 4(A), 4(B), 4(C), 5(A), 5(B), and 5(C)). No bacteria were observed on the surface membrane.

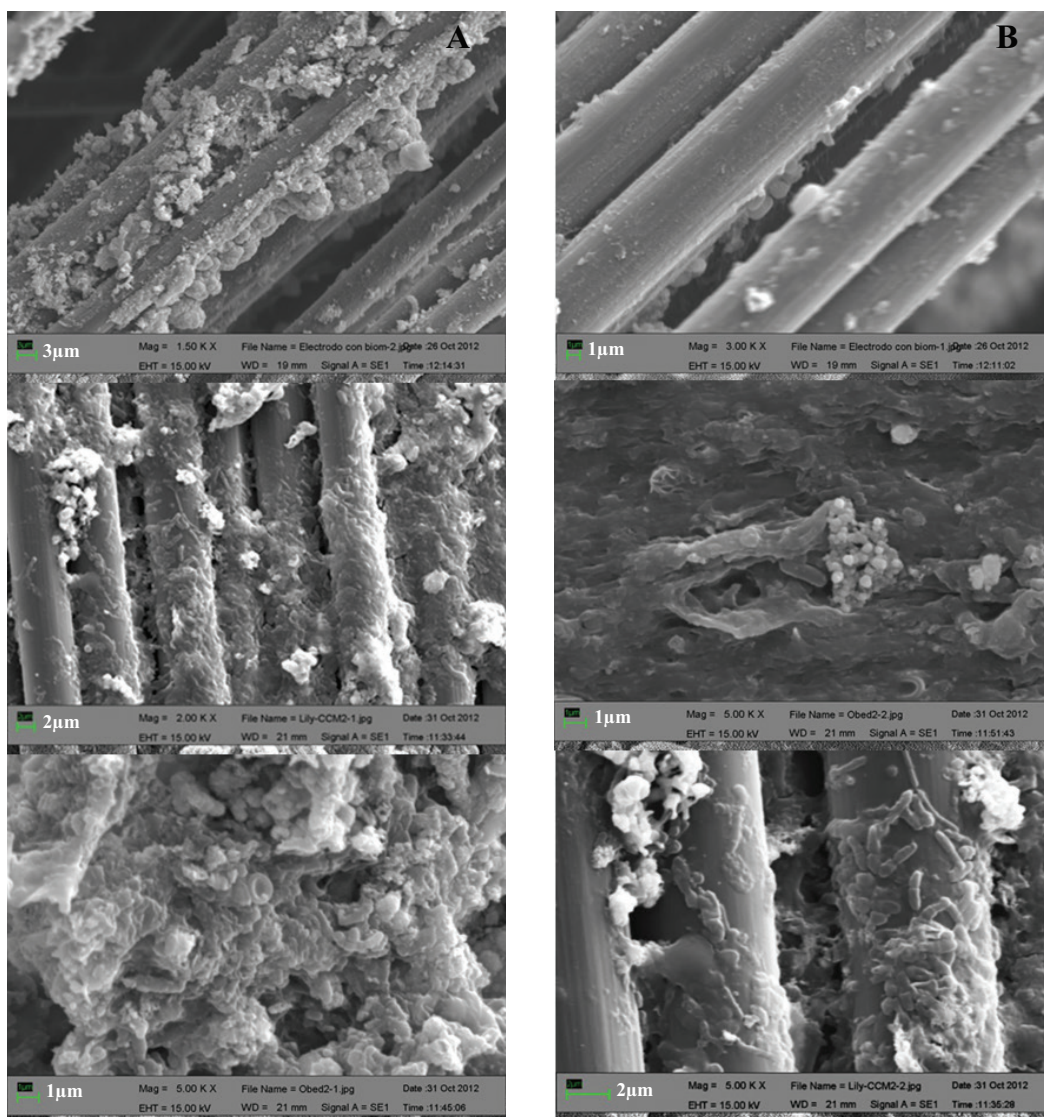


Fig. 3. SEM images from anodes after the end fed-batch cycles of the MFCs: (A) MFC1; (B) MFC2.

The SEM-EDX analysis for CEM virgin consisted of 61.1% carbon, 23.3% oxygen, 10.9% sulfur, and 4.6% sodium.

The MFC1 without recirculation (R1), the EDX spectrum showed salts precipitated of calcium (Ca), phosphorus (P), and magnesium (Mg) with a weight percent of 17.2%, 11.3% and 0.9%, respectively (Fig. 4(A1) and 4(A2)) on the surface membrane. For the membrane with a flow recirculation of  $74 \text{ mL min}^{-1}$  (R2), corresponding elements in weight percentage of 0.8% Mg, 4.5% P and 10% Ca (Fig. 4(B1) and 4(B2)) were detected. Inorganic elements found for a flow recirculation of  $152 \text{ mL min}^{-1}$  (R3) were 1.13% Mg, 6.7% P and 2.3% Ca among other elements (iron, potassium, and aluminum) (Fig. 4(C1) and 4(C2)). According to the EDX spectrum and SEM micrographs, increasing the flow recirculation in the MFC1 decreased the concentrations of Ca and P on the surface of the membranes. Precipitated salts on the surface of CEM of MFC1 concerning to struvite crystals ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) was identified. This struvite crystal was generated by removing ammonia nitrogen and phosphorus from the liquid phase

pig wastewater. Struvite formation was detected in the three operating conditions of the MFC1 (Fig. 4(A1), 4(B1), and 4(C1)). Struvite crystals were irregular with a double flat face smooth texture and triclinic structure, so that crystallization and precipitation of struvite adding alkaline compounds was required. In this case, the presence of Ca and Mg ions in the pig wastewater (removed and precipitated at the cathode) and environmental conditions of the MFC1 (ORP  $-150$  and  $-267 \text{ mV}$  and slightly alkaline pH (7.6–7.8)) generated the formation of struvite crystals. Ichihashi and Hirooka [11] suggest that the precipitation of struvite on the cathode is because the pH near the electrode was higher than in the liquid suspension of the MFC. Recently, few studies have shown the formation of struvite in MFCs using digested sludge as substrate [37] and wastewater [11].

For the MFC2, inorganic elements found in the membranes for the different operating conditions were Ca and P in the form of calcium phosphate crystals (Fig. 5(A1), 5(B1) and 5(C1)). For R1, the weight percent of P and Ca were 11%

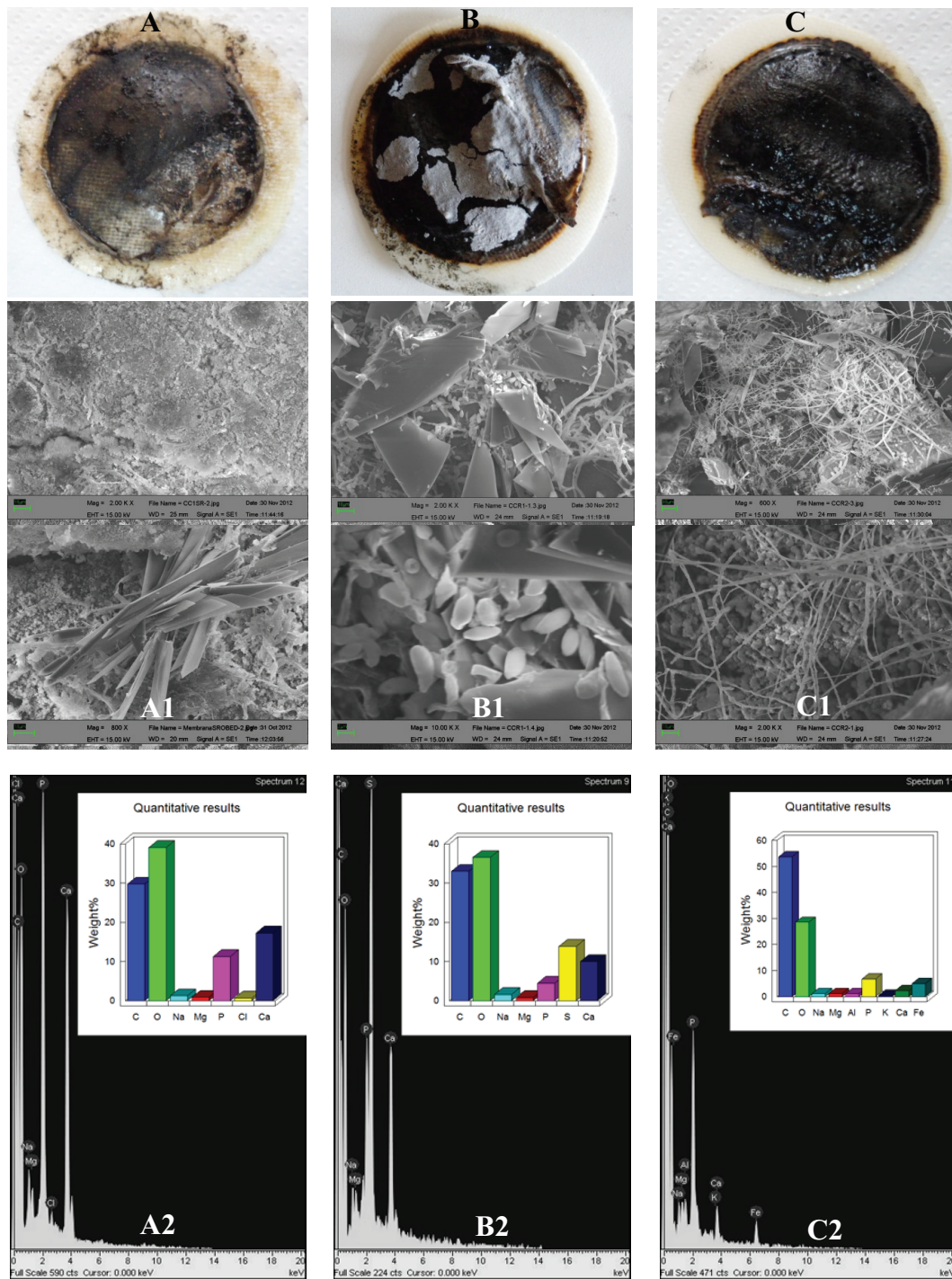


Fig. 4. Fouling CEM after the end fed-batch cycle of the MFC1 fed with pig slurry. (A) fouled image CEM without flow recirculation (R1); (A1) SEM morphology image showing precipitate struvite over membrane surface; (A2) EDX spectrum fouled membrane. (B) Fouled image CEM with flow recirculation of the 74 mL min<sup>-1</sup> (R2); (B1) SEM morphology image showing precipitate salts over membrane surface; (B2) EDX spectrum fouled membrane. (C) Fouled image CEM with flow recirculation of the 152 mL min<sup>-1</sup> (R3); (C1) SEM morphology image showing precipitate salts over membrane surface; (C2) EDX spectrum fouled membrane.

and 28.3%, respectively (Fig. 5(A2)). In the CEM for R2 condition, the weight percent of Ca and P was 14.8% and 20.6%, respectively (Fig. 5(B2)). For R3, phosphorus not was found but if Mg (1.2%) and Ca (0.8%) (Fig. 5(C2)). Struvite was not

was found in the MFC2, due to the composition and concentration of the compounds of SWW. As in MFC1, by increasing the flow recirculation, the amount of Ca and P ions was diminished in the MFC2.

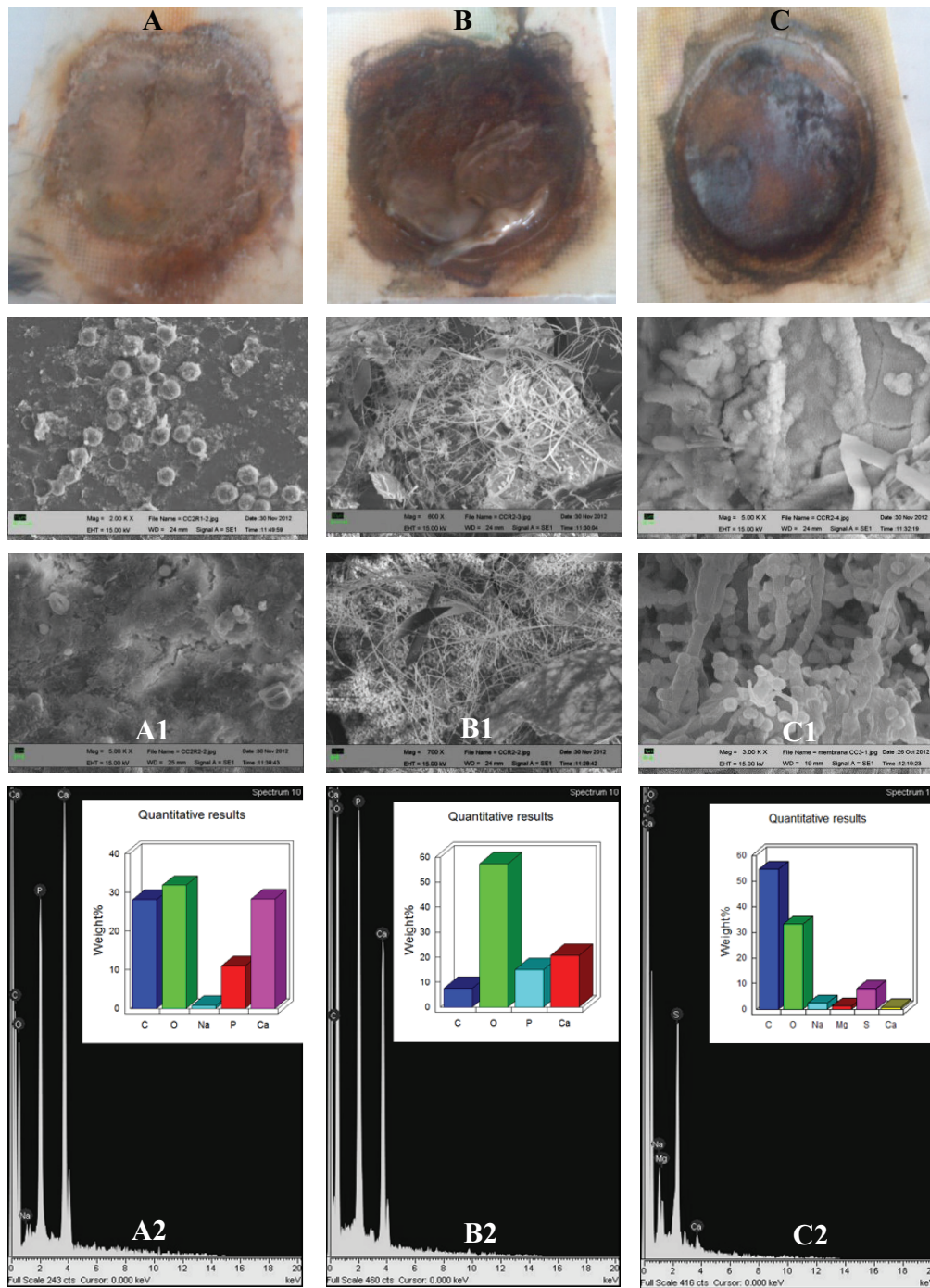


Fig. 5. Fouling CEM after the end fed-batch cycle of the MFC2 fed with synthetic wastewater. (A) Fouled image CEM without flow recirculation (R1); (A1) SEM morphology image showing precipitate salts over membrane surface; (A2) EDX spectrum fouled membrane. (B) Fouled image CEM with flow recirculation of the 74 mL min<sup>-1</sup> (R2); (B1) SEM morphology image showing precipitate salts over membrane surface; (B2) EDX spectrum fouled membrane. (C) Fouled image CEM with flow recirculation of the 152 mL min<sup>-1</sup> (R3); (C1) SEM morphology image showing precipitate salts over membrane surface; (C2) EDX spectrum fouled membrane.

#### 4. Conclusions

Simultaneous energy recovery with COD removal, nitrification-denitrification process, and phosphorus removal was accomplished in a single-chamber batch mode air cathode MFC using pig slurry as carbon source. It was found

that the mixing intensity into MFCs affected the contaminant removals, power densities, internal resistances, coulombic efficiencies, experimental energies, and the operational cycles of MFCs. Voltages across 1,200 ohm external resistance in the ranging from 31 mV to 234 mV were achieved in the MFCs.



The voltages generated in MFC1 (fed with pig slurry) were higher compared with the voltages obtained from MFC2 (fed with synthetic water). The maximum power densities obtained from MFC1 and MFC2 were 27.7 and 3.8 mW m<sup>-2</sup> corresponding to current densities of current density of 118 and 53.4 mA m<sup>-2</sup>, respectively. The turbulence generated by flow recirculation decreased the inorganic concentrations on the membrane surfaces causing detachment of the salts deposited on the membranes of the MFCs.

### Acknowledgment

Financial support was provided by SEP-CONACYT, Project No. CB-2013/221433.

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