



## Electricity from landfill leachate using microbial fuel cells: Comparison with a biological aerated filter

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### ABSTRACT

Four experimental columns were employed in this study to investigate their performance under wastewater treatment conditions. One column was set-up as a biological aerated filter and the remaining three were set-up as microbial fuel cells (MFCs), two of which were connected to an external load whereas the third was left open circuit. The performance of the columns under several flow rates and leachate strengths was studied in terms of BOD<sub>5</sub> removal efficiencies and electricity generation, when a fixed resistive load was connected. Results obtained demonstrated that it is possible to generate electricity and simultaneously treat landfill leachate in MFC columns. Energy generation in MFC columns improved with increasing flow rates from 24 to 192 mL/h, while BOD<sub>5</sub> removal efficiency levels reached a maximum at 48 mL/h and dropped to relatively low values at higher flow rates. The maximum removal efficiencies were obtained at a loading rate of 0.81 kg BOD<sub>5</sub>/m<sup>3</sup> d for columns C1, C2 and C4 and 1.81 kg BOD<sub>5</sub>/m<sup>3</sup> d for column C3. Electrical output levels and BOD<sub>5</sub> concentrations at the MFC columns showed a linear relationship, which allows the system to be used as a BOD<sub>5</sub> sensor. Part of the BOD removal was not associated with power generation and was attributed to the presence of alternative end terminal electron acceptors and volatilisation. The MFC columns could reach the same or even higher removal efficiencies than those from the biological aerated filter with the advantage of producing energy and saving cost of aeration. To the best of the authors' knowledge, this is the first study that compares the MFC technology with other conventional treatment systems for removing pollutants from wastewater.

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### 1. Introduction

The generation of leachate is one of the main environmental problems associated with the removal of waste at landfills. It is produced after the percolation of water through decomposing wastes. Leachates are heavily polluted wastewaters with a complex composition containing four groups of pollutants: dissolved organic matter, inorganic macro-components, heavy metals, and xenobiotic organic compounds [1]. This complex composition and the variance in quality and quantity usually observed [2], make leachate one of the most difficult of wastewaters to be treated. All kinds of leachate treatment options have been reported such as leachate recirculation [3], co-treatment with domestic wastewater [4], physico-chemical systems [5], biological processes [6] or combined treatments [7].

Amongst the biological processes found in the scientific literature, submerged biological filters have shown good removal efficiencies in treating leachate [8–10]. However, as is the case with conventional treatment systems, this method consumes energy during the treatment process.

A microbial fuel cell (MFC) is a device that generates electrical energy from the catalytic reaction of anaerobic oxidation of organic matter (bio-chemical energy) by microorganisms [11,12]. Furthermore, MFCs can be used as biological oxygen demand (BOD) sensors as there is a direct relationship between the current generated and the BOD<sub>5</sub> concentration [13–15]. This allows for better control of the treatment plant by providing real time monitoring without the need for waiting the 5 days required by the conventional method. The microbial fuel cell (MFC) technology is still at an early stage of development, but shows great potential as a new method to accomplish both wastewater treatment and electricity generation [16,17].

Different kinds of wastewater have been treated with MFCs. The current and power density, coulombic efficiency and pollutants removal efficiencies differ between the various studies according

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to the experimental conditions (initial wastewater composition, concentration, and MFC set-up conditions). Habermann and Pommer [16] mentioned the COD removal of a landfill effluent by an MFC, though they did not report values of energy generation with that effluent. You et al. [18] demonstrated that complex organic pollutants found in leachate could also serve as substrate for a dual-chamber or a single-chamber MFC to generate electricity. More recently, Zhang et al. [19] reported on an upflow air-cathode membrane-free microbial fuel cell that could continuously generate electricity from leachate for 50 h. However, to the best of the authors' knowledge the MFC technology has not previously been compared with other conventional treatment systems for removing pollutants from wastewater.

The objective of the present work was to study the feasibility of MFC systems fed with landfill leachate in terms of energy production, BOD removal efficiencies and also the possible use of the system as a BOD sensor. The effect of the flow rate and the leachate strength on the MFC performance was compared to those of a biological aerated filter.

## 2. Materials and methods

### 2.1. Landfill leachate origin and sampling

Leachate samples were taken from Harnhill Landfill site, which is situated in South Gloucestershire, approximately 10 km to the north of Bristol, UK. Landfilling was developed in four phases from 1966 to 2003 in a former limestone quarry. The majority of the disposed waste was domestic although it also received commercial waste similar in nature to domestic waste. Only the leachate produced in the last phase (filled between 1997 and 2003) was obtained.

For leachate characterisation, samples were collected from boreholes Y3 and Y5 and from tower 3 (all located within phase 4 of the landfill) at different dates, from September 2005 to January 2006 in plastic carboys and transported to the laboratory for analysis. Leachate samples extracted on the 25th of January 2006 from tower 3 were employed for the column experiments.

### 2.2. Laboratory scale plant description

The plant consisted of four columns (Fig. 1). Two of these columns (C1 and C2) were setup as MFCs with electrode materials. A third column (C3) was built as a biological aerated filter (control), packed with ceramic brick pieces. The last column (C4) was also set-up as an MFC with electrode material, but left open circuit with the aim of determining the BOD<sub>5</sub> removal not associated with energy generation.

The columns were made from 1 L-plastic measuring cylinders with a total height of 41.7 cm and an internal diameter of 6 cm. The working volume of each column was

0.9 L. The MFC columns comprised two chambers: anode and cathode. The anode consisted of units of carbon veil electrode (PRF Composite Materials Poole, Dorset, UK) of 360 cm<sup>2</sup> surface area, folded down to a suitable size (12-folds of 10 cm × 3 cm). The electrode was connected to the outside load using platinum wire that was threaded through the folds. This shape maximised the total projected surface area of electrode to the leachate, and when inserted into the bioreactor compartment, together became the anodic chamber.

Seven small holes distributed at the nodes and centre of a hexagon of 1 cm diameter were drilled through the bioreactor wall towards the bottom. This provided the interface for the fixing of a proton selective membrane, which acted as the proton bridge with the cathode. A cation exchange membrane (Merch Ltd., Lutterworth, UK) with a 30 cm<sup>2</sup> surface area was placed over the group of holes. A carbon veil electrode (laminated to help maintain moisture) was placed on the outer side of the proton selective membrane (PEM) as the cathode with a surface area of 360 cm<sup>2</sup>-folded down to a 3D structure of 3 cm × 5 cm × 1 cm in order to reduce the resistivity of the material. The PEM and the carbon veil were held in place over the group of holes with rubber gaskets and cable ties. Platinum wire was used to connect the electrode material.

The MFC was linked to the serial communications port of a desktop pc via an 8-channel RS232 interface connected to an ADC-16 A-D converter (Pico Technology Ltd., Cambridgeshire, UK). This allowed the electrical current between the anode and cathode to be monitored in real time.

Real time data were recorded using PicoLog<sup>®</sup> v. 5.09.4 recorder software and retrieval of the data was performed using the PicoLog<sup>®</sup> v. 5.09.4 player software (Pico Technology). Data points were recorded every 5 minutes and electrode output was measured in millivolts (mV) against time, but expressed as current and power.

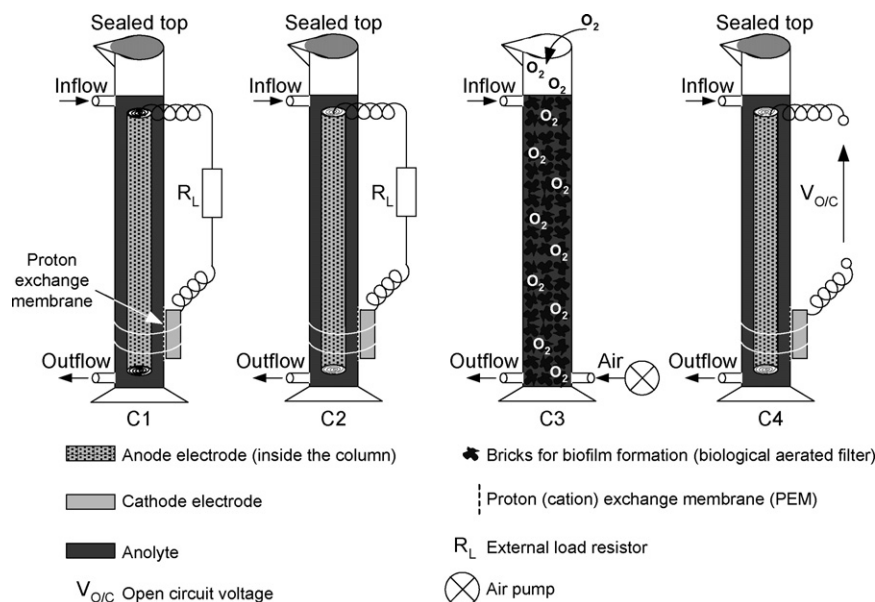
Current  $I$  in amperes (A) was calculated using Ohm's law,  $I = V/R$ , where  $V$  is the measured voltage in volts (V) and  $R$  is the known value of the external load resistor in Ohms ( $\Omega$ ). From this, it was possible to calculate the power output  $P$  in watts (W) of the MFCs since  $P = I \times V$ . Current density was calculated using  $I = (V/\alpha R)$ , and power density was calculated using  $P = I \times (V/\alpha)$ , where in both cases  $\alpha$  is the electrode surface area in m<sup>2</sup>.

For maintaining electrode moisture, the cathode was periodically hydrated (2–3 times every day) with 3 mL of K<sub>3</sub>Fe(CN)<sub>6</sub> (32.88 g L<sup>-1</sup>) mixed with K<sub>2</sub>HPO<sub>4</sub> (87.09 g L<sup>-1</sup>), pH 7.5. The frequency of moistening was dictated by the MFC output.

A multi-channel peristaltic pump (Watson Marlow<sup>®</sup> 205U, 12 channels) was used to feed the leachate to the top of each column and re-circulate some of the treated leachate (200%) back into the columns. Every 24 h, leachate samples (50 mL) were collected from the inlet and the outlet of each column for the different analyses.

For the system start up, column C1 and column C4 (control) were inoculated with leachate + sludge (200 mL of sludge and 600 mL of leachate diluted 1:2 with distilled water and adjusted to pH 7 with 1 M phosphoric acid). The activated sludge was taken from the Avonmouth sewage treatment works. Columns C2 and C3 (biological aerated filter) were filled with leachate-diluted 1:2 and adjusted to pH 7 with phosphoric acid (1 M).

The MFC columns (C1 and C2) were kept in batch mode for 4 days during which time the external load resistance was progressively reduced from 2000 to 1000  $\Omega$  and finally to 500  $\Omega$  in order to achieve maximum power transfer which occurs at half the open circuit value [20]. The system was then changed to continuous mode



**Fig. 1.** Schematic diagram of the experimental setup with the 4 columns: C1 and C2 (working MFCs), C3 (biological aerated filter; control 1), C4 (open circuit MFC; control 2). Parts are labelled in the guide below the diagram.

at a flow rate of 24 mL/h using leachate-diluted 1:4 (adjusted to pH 7). After 4 days, the leachate strength at input was switched to 1:8. The internal recirculation for the MFC columns was set at 200% in order to maintain the same conditions as column C3 (biological aerated filter). The recirculation also helped maintain mixing and a better migration of protons (and hence electrons) from the anode to the cathode [21].

### 2.3. Analytical methods

In order to perform COD and BOD<sub>5</sub> analyses, the samples were centrifuged for 5 min at 2500 rpm. There were very little differences between centrifuged and non-centrifuged samples. COD was determined according to the closed reflux method (colorimetric), while BOD<sub>5</sub> followed the dilution method (iodometric, azide modification). Both methods are included in the Standard Methods for the Examination of Water and Wastewater [22]. COD analysis was performed as part of the characterisation process of the landfill leachate (see Table 1) but was also performed on the samples collected daily from the experimental columns (data not shown).

Ion concentration (pH) and redox potential (Eh) were monitored with a pH meter (Sartorius PT-10) while conductivity was measured with a multi-range conductivity meter (HANNA Instruments HI 9033). Heavy metals (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) and cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Varian® VISTA-PRO CCD, Simultaneous ICP-OES). Heavy metals analysis followed the method of standard additions and samples were previously digested with nitric acid. For the cation analyses the samples were diluted 1:100, acidified (2% nitric acid) and filtered prior to the ICP-OES analysis. Anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup>) were determined by ion chromatography (Dionex® QIC) after centrifugation and 1:100 dilution.

### 2.4. Statistical analysis

The data were statistically analysed using SPSS for Windows 14.0. An analysis of variance (ANOVA) test with a significance level of 5% ( $P < 0.05$ ) was used to assess the differences amongst the various values of the variables tested.

## 3. Results

### 3.1. Leachate characterisation

The leachate showed high COD and BOD<sub>5</sub> concentrations and its pre-treatment strength varied depending on the borehole and the date of sampling. COD and BOD<sub>5</sub> concentrations were in the range of

12,900–35,300 mg/L and 5800–18,000 mg/L, respectively and the highest concentrations were measured at the leachate samples extracted from borehole Y3. The BOD<sub>5</sub>/COD ratio (or biodegradability factor) indicates the biodegradability of the organic matter contained in the leachate samples [2,23]. This relationship varies from 0.5 for young leachates to 0.2 for older (more stabilised) leachates [2]. In the samples analysed, this ratio varied between 0.34 and 0.57 and all samples had a relatively high biodegradability index. Table 1 shows the results of the analyses performed on the raw leachate samples.

Total suspended solids TSS concentration was high (in the range of 403–950 mg/L) due to the leachate samples being extracted directly from the bottom of the landfill in contact with the wastes without any sedimentation processes. Nitrate and nitrite concentrations were generally low, in the range of 8.1–13.1 mg/L and 9.8–27.9 mg/L, respectively. This was attributed to the predominant anaerobic conditions of the landfill site [24], probably at the methanogenic phase of decomposition. Ammonia nitrogen was not analysed in this study, however previous analyses made by the site managers showed high ammonia concentrations, in the range of 2200 and 3800 mg/L [25]. This would indicate that most of the nitrogen is in the form of ammonia which is typical of landfill leachates [2]. Amongst the different ions analysed, the highest concentrations were measured for chloride (733–3806 mg/L), sodium (2654–3081 mg/L), and potassium (1265–1609 mg/L).

The pH of the leachate samples was alkaline varying between 7.74 and 8.86, which again are typical values for the methanogenic phase of decomposition [1].

Oxidation–reduction potential values ranged from –91.50 to –31.70 mV, which reflect the degree of anaerobiosis of the leachate [23]. Conductivity was also high with values between 23.60 and 33.80 mS/cm, due to the high levels of inorganic ions in the samples [26].

Different heavy metals (arsenic, cadmium, chromium, copper, lead, manganese, mercury, nickel, zinc, silver and cobalt) were also detected though at low concentrations.

**Table 1**  
Results of the main Harnhill landfill leachate parameters analysed. Samples were collected at different dates from different boreholes.

Date of sampling, borehole	26/09/2005, Y3	02/11/2005, Y3	07/11/2005, Tower 3	14/11/2005, Y5	21/11/2005, Tower 3	25/01/2006, Tower 3
T (°C) (at the moment of sampling)	58	53	55	52	54	–
COD (mgO <sub>2</sub> /L)	31,800	35,300	16,933	27,267	19,633	12,900
BOD <sub>5</sub> (mg O <sub>2</sub> /L)	18,000	17,650	5,800	13,633	10,500	6,300
TSS (mg/L)	–	403.0	707.5	–	950.0	–
F <sup>-</sup> (mg/L)	133.6	136.0	54.9	–	89.4	–
Cl <sup>-</sup> (mg/L)	2681.8	3383.3	3806.4	–	733.9	–
NO <sub>2</sub> <sup>-</sup> (mg/L)	20.2	22.8	27.9	–	9.8	–
NO <sub>3</sub> <sup>-</sup> (mg/L)	9.8	13.1	8.1	–	9.7	–
PO <sub>4</sub> <sup>3-</sup> (mg/L)	38.5	29.6	39.3	–	47.7	–
SO <sub>4</sub> <sup>2-</sup> (mg/L)	199.0	149.6	16.7	–	38.2	–
Na <sup>+</sup> (mg/L)	–	–	3081.8	–	2654.6	–
K <sup>+</sup> (mg/L)	–	–	1609.2	–	1265.2	–
Ca <sup>2+</sup> (mg/L)	–	–	90.0	–	84.1	–
Mg <sup>2+</sup> (mg/L)	–	–	96.1	–	81.8	–
Ag (mg/L)	–	–	0.02	–	0.02	–
As (mg/L)	–	–	0.37	–	0.97	–
Cd (mg/L)	–	–	0.01	–	0.01	–
Co (mg/L)	–	–	0.14	–	0.12	–
Cr (mg/L)	–	–	0.52	–	0.53	–
Cu (mg/L)	–	–	0.16	–	0.07	–
Fe (mg/L)	–	–	19.4	–	13.6	–
Hg (mg/L)	–	–	0.07	–	0.02	–
Mn (mg/L)	–	–	0.31	–	0.30	–
Ni (mg/L)	–	–	0.36	–	0.36	–
Pb (mg/L)	–	–	0.04	–	0.13	–
Zn (mg/L)	–	–	0.55	–	1.51	–
pH	8.21	8.35	8.00	8.86	8.30	7.74
Eh (mV)	–59.0	–64.7	–45.2	–91.5	–61.1	–31.7
Conductivity (mS/cm)	23.6	26.4	33.8	30.1	28.7	33.3

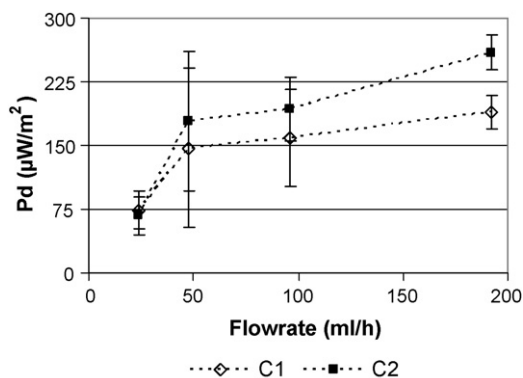


Fig. 2. Mean power density recorded at the different flow rates tested (24, 48, 96 and 192 mL/h) for the working MFC columns (C1 and C2).

The leachate also contained different xenobiotic organic compounds (phenols and cresols, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, phthalates and furans) though at low concentrations (data not shown).

The leachate showed a brown-reddish dark colour which can be attributed to the presence of iron [26] and humic substances [2,27]. The leachate had a strong odour, probably due to a high content of volatile fatty acids [28].

### 3.2. System start up

Landfill leachates contain different microbial communities [29–32]. The MFC column inoculated with leachate + sludge (C1) initially produced higher levels of current, however the MFC column inoculated with only leachate (C2) subsequently started to perform better. This could be due to the column inoculated with landfill leachate needing a longer acclimation period than the column inoculated with activated sludge, or it could also be that sludge was utilised as fuel. These results suggest that there is no need to inoculate the MFC with activated sludge in order to produce useful output levels, since leachate must naturally contain sufficient electrogenic (or anodophilic) microorganisms to colonise the electrode.

### 3.3. Influence of the flow rate on the performance of the columns

The effects of four different flow rates (24, 48, 96 and 192 mL/h) on MFC power output and BOD<sub>5</sub> removal efficiency were investigated with leachate diluted 1:8. The results for columns C1 and C2 are shown in Fig. 2. The bars indicate the standard deviation of the values obtained during the time recorded.

As shown in Fig. 2, the power density improved with increasing flow rate. The column inoculated with leachate (C2) produced slightly better results than the column inoculated with activated sludge (C1). The maximum values were obtained for both columns at a flow rate of 192 mL/h, with an average energy generation of  $3.24 \pm 0.17$  mA/m<sup>2</sup> ( $188.91 \pm 19.48$  μW/m<sup>2</sup>) for col-

umn C1 and  $3.79 \pm 0.15$  mA/m<sup>2</sup> ( $259.37 \pm 20.29$  μW/m<sup>2</sup>) for column C2. The BOD<sub>5</sub> results of these experiments are summarised in Table 2.

Fig. 3 shows the BOD<sub>5</sub> removal efficiency as a function of flow rate (a), hydraulic retention time (b) and loading rate (c) for all four columns. As can be seen in Fig. 3a higher efficiencies were recorded at lower flow rates, with a maximum at 48 mL/h, at which point the average efficiencies were ~57% for columns C1 and C2 and ~66% for columns C3 and C4. Further increases in the flow rate had an adverse effect on BOD<sub>5</sub> removal efficiencies, for all columns.

A similar effect was observed when BOD<sub>5</sub> removal efficiency was plotted against the loading rate (Fig. 3c). The maximum removal efficiencies were obtained at a loading rate of 0.81 kg BOD<sub>5</sub>/m<sup>3</sup> d for columns C1, C2 and C4 and 1.81 kg BOD<sub>5</sub>/m<sup>3</sup> d for column C3. This was probably due to the lower working volume of C3 when compared to C1, C2 and C4, which was a result of the inclusion of support material (pieces of bricks).

Higher BOD<sub>5</sub> removal efficiencies were also produced at higher hydraulic retention times (HRTs) as can be seen in Fig. 3b. The maximum efficiency levels were produced at a hydraulic retention time of 18.75 h for columns C1, C2 and C4 and 8.33 h for column C3. Higher retention times than those at which maximum efficiency was recorded, did not further improve the removal efficiencies.

The results for pH, Eh and conductivity measured for both the inlet and outlet samples of columns C1, C2, C3 and C4 at the different flow rates are also shown in Fig. 3(d, e, and f). The highest variance in pH, Eh and conductivity with respect to the inlet leachate was measured from column C3 (aerated).

The pH of the leachate increased at the outlet of all the columns. The maximum difference with respect to the pH of the inlet leachate coincided – for the majority of the cases – with the flow rates at which the maximum BOD<sub>5</sub> removal efficiencies were obtained. For columns C1, C2 and C4 the increase in pH was only between 0.11 and 0.17 units. For column C3, however, this increase was found to be between 0.68 and 0.82 units.

A similar behaviour was observed with respect to the Eh values but in the opposite way, due to the inverse relationship between pH and Eh. In this case the Eh values of the leachate decreased to more negative values after going through the columns. The maximum decrease in the values of Eh was around 10 mV for columns C1, C2 and C4, whereas for column C3 the decrease in Eh reached 49.5 mV (from –31.7 to –81.2 mV).

The conductivity values of the outlet leachate of columns C1, C2 and C4 increased slightly with respect to the inlet leachate whereas for column C3 a small decrease was observed (between 0.5 and 1.31 mS/cm).

### 3.4. Leachate strength influence

Different leachate concentrations (1:8, 1:4, 1:2 and full strength) were investigated by diluting the neat leachate with distilled water. The flow rate was kept constant at 96 mL/h, allowing a rapid replacement of the anolyte with new leachate.

Table 2

BOD<sub>5</sub> results of the experiments at different flow rates: hydraulic load, hydraulic retention time, BOD<sub>5</sub> loading rate and BOD<sub>5</sub> measured at both the influent and effluent of each column.

Flow rate (mL/h)	Hydraulic load (m <sup>3</sup> /m <sup>2</sup> d)	Hydraulic retention time (h)		BOD <sub>5</sub> loading rate (kg BOD <sub>5</sub> /m <sup>3</sup> d)		BOD <sub>5</sub> influent (mg/L)	BOD <sub>5</sub> effluent (mg/L)			
		C1, C2, C4	C3	C1, C2, C4	C3		C1	C2	C3	C4
24	0.2	37.5	16.7	0.3	0.7	468	222	265	255	244
48	0.4	18.7	8.3	0.8	1.8	630	269	270	210	210
96	0.8	9.4	4.2	1.4	3.2	555	540	480	420	510
192	1.6	4.7	2.1	2.9	6.6	572	555	525	501	564

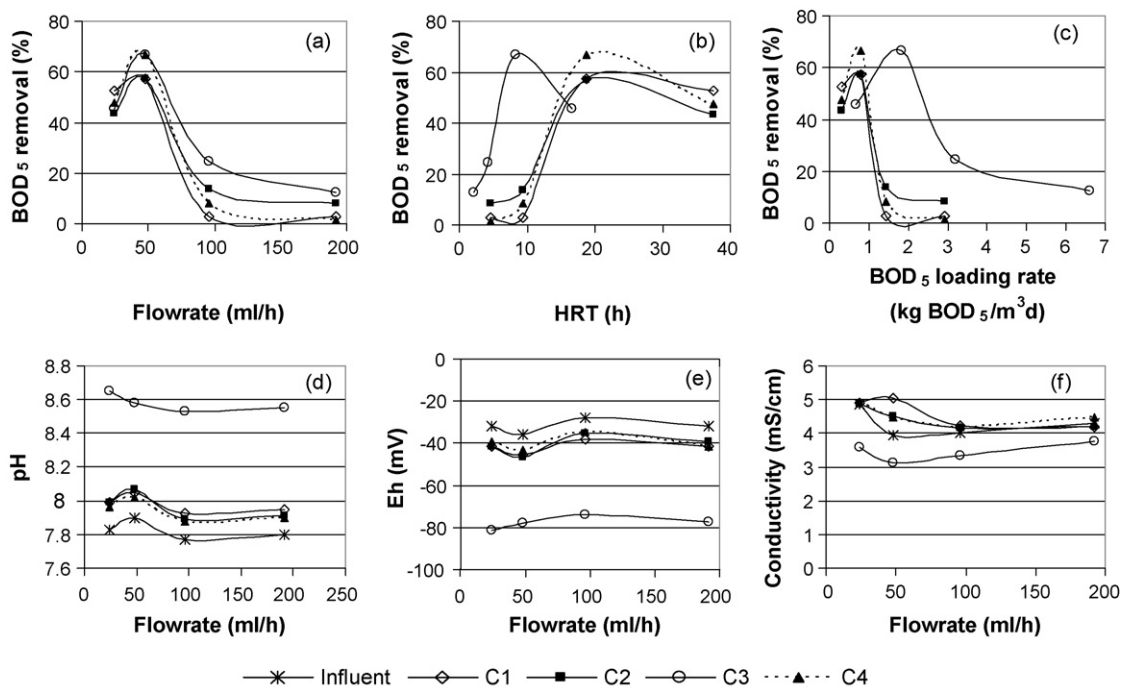


Fig. 3. BOD<sub>5</sub> removal efficiencies for the four columns as a function of (a) flow rate, (b) hydraulic retention time and (c) loading rate, together with (d) pH, (e) redox potential (Eh) and (f) conductivity measured at the inlet and outlet of each column at the different flow rates tested.

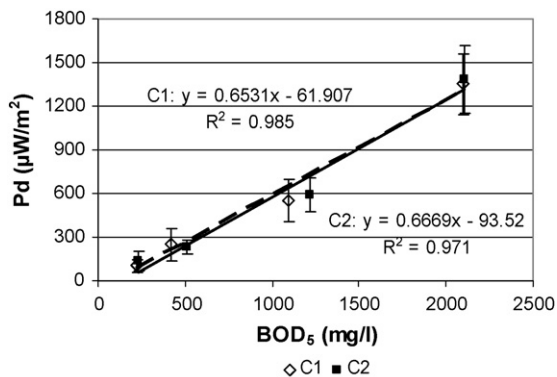


Fig. 4. Power density generated as a function of BOD<sub>5</sub> of the columns' effluent for the two working MFC columns (C1 and C2). Data points represent the mean power density values and the dotted lines represent the linear regression fit shown with their equations.

Fig. 4 shows power density generated as a function of the BOD<sub>5</sub>. A linear correlation ( $R^2 = 0.971$ ) was found between the output measured in the columns and the BOD of the leachate inside the columns. Power density increased linearly with the leachate strength. Columns C1 and C2 showed similar results, with column

C1 having a slightly better fit. There were significant statistical differences between the different leachate strengths tested for power and power density ( $P < 0.05$ ). The highest power density values were obtained with full strength leachate, with a mean of  $1.35 \pm 0.21$  mW/m<sup>2</sup> for column C1 and  $1.38 \pm 0.24$  mW/m<sup>2</sup> for column C2.

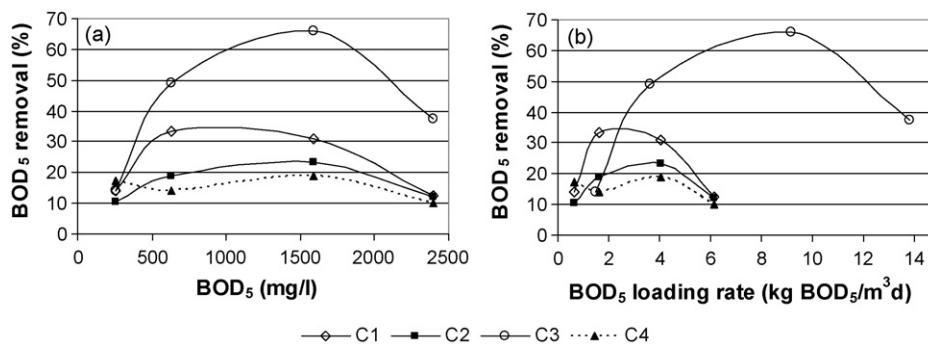
Table 3 summarises the results of leachate treatment at different leachate strengths whereas Fig. 5 illustrates the BOD<sub>5</sub> removal efficiencies as a function of leachate strength and of loading rate. The relationship between the leachate strength and the removal efficiencies was not linear. MFC columns (C1 and C2) showed low BOD<sub>5</sub> removal (<34%BOD<sub>5</sub>). The highest BOD<sub>5</sub> removal efficiency was obtained with column C3 (biological aerated filter), with a maximum 66% when it was fed with leachate diluted 1:2. However, as shown in Fig. 5 this column received higher volumetric loadings due to a smaller working volume.

The greatest differences in pH, Eh and conductivity with respect to the inlet leachate were measured for column C3 (aerated), across all flow rates. The effluent pH and Eh values of columns C1, C2 and C4 were similar to those of the inlet leachate, whereas that of column C3 increased by 0.66 and 0.82 units and the Eh dropped by 40.7 and 49.5 mV (absolute values), since the conditions became more reducing.

Conductivity values measured at the outlet of column C1 were also similar to those of the inlet leachate sample. Columns C2 and

**Table 3**  
BOD<sub>5</sub> results obtained for columns 1, 2, 3 and 4, working at different leachate strengths: hydraulic load, hydraulic retention time, BOD<sub>5</sub> loading rate and BOD<sub>5</sub> measured at both the influent and effluent of each column.

Leachate (dilution)	Hydraulic load (m <sup>3</sup> /m <sup>2</sup> d)	Hydraulic retention time (h)		BOD <sub>5</sub> loading rate (kg BOD <sub>5</sub> /m <sup>3</sup> d)		BOD <sub>5</sub> influent (mg/L)	BOD <sub>5</sub> effluent (mg/L)			
		C1, C2, C4	C3	C1, C2, C4	C3		C1	C2	C3	C4
1:8	0.8	9.4	4.2	0.7	1.5	258	222	231	222	213
1:4	0.8	9.4	4.2	1.6	3.6	630	420	510	320	542
1:2	0.8	9.4	4.2	4.1	9.2	1590	1096	1217	540	1290
Full strength	0.8	9.4	4.2	6.1	13.8	2400	2100	2108	1500	2160



**Fig. 5.** BOD<sub>5</sub> removal efficiencies for the two working MFC columns (C1 and C2), the biological aerated filter (C3; control 1) and the open circuit MFC (C4; control 2) as a function of (a) leachate strength and (b) loading rate.

C4 showed similar results with the highest removal efficiencies of around 47% obtained with full strength leachate. Column C3 also showed the highest conductivity removal efficiency (56%) when percolated with full strength leachate

#### 4. Discussion

The greatest significance of this work is that it compares the MFC technology and the biological aerated filter based on exactly the same leachate and under identical operating conditions and configuration. Results obtained previously from other workers would be very difficult to compare with, as the characteristics of the leachates tend to vary. The difference in the effective volume of the two systems was due to the different properties of the support material of the biological aerated filter as well as the aeration. Comparing the biological aerated filter and the MFC, even though results were normalised according to the different volumes, the MFC system (energy producing) could reach equivalent removal efficiencies as those obtained from the biological aerated filter (energy consuming). If adopted on a larger scale, this could save on energy costs.

##### 4.1. Effects of the flow rate and hydraulic retention times on the performance of the MFC columns

Although COD analyses were performed (results not shown) we have focused more on the BOD<sub>5</sub>, which is present at a fixed ratio of COD (and indeed both parameters followed similar patterns), for evaluating removal efficiency. In this study we observed that for low flow rates (<48 mL/h) energy generation improved in relation to increasing flow rates, with a maximum output recorded at 48 mL/h. No significant improvements were recorded at higher flow rates.

A more profound response was observed for the hydraulic retention time (HRT), which proved to be a more influential parameter since it increased the BOD<sub>5</sub> removal efficiency by sixfold, after it was merely doubled. This suggests that the influent exposure time in the anodic MFC chamber can be a vital design parameter for future wastewater treatment systems and more clearly showed the direct relationship between power output and removal efficiencies.

The pH increase observed at the outlet of all the columns could be attributed to the removal of acid components present in the leachate such as volatile fatty acids. The higher pH difference for the effluent of column C3 may be due to aeration, as previously described [33].

These experiments were conducted without pH adjustment. If no buffer solution is used in a working MFC, theoretically there will be no pH shift when the reaction rate of protons, electrons and

oxygen at the cathode equals the production rate of protons at the anode [34]. However, as previously shown, a slow proton exchange rate through the membrane, results in higher pH shifts [12]. Gil et al. [12] detected a pH difference of 4.1 (9.5 at the cathode and 5.4 at the anode) after a 5-h operation with an initial pH of 7 without buffering. With the addition of a phosphate buffer (50 mM, pH 7.0 with 100 mM NaCl) to the anode and cathode, pH shifts at both the cathode and anode were less than 0.5 units and the current output increased by about one- to two-fold. These results showed that proton transport through the membrane was slower than its production rate in the anode and its consumption rate in the cathode compartments. The added buffer compensated the slow proton transport rate and improved the proton availability for the cathodic reaction. In our experiments, only a slight pH increase was observed in the MFC columns and the final pH was kept below 8.1. This suggests that a good rate of proton transport was maintained through the membrane.

The high conductivity of the leachate could favour the MFC performance. Liu et al. [35] increased power by up to 85% by adding NaCl (300 mM) to the solution in the anode chamber. This was possibly due to the fact that NaCl enhanced the conductivity of the anolyte. Heilmann and Logan [36] also observed that the maximum power density increased by 33% when their sample was supplemented with NaCl.

##### 4.2. Leachate strength influence

The influence of BOD<sub>5</sub> (and thus COD) is usually modelled with a Monod-type kinetic equation, where the half-rate constant is usually small. This means that the BOD<sub>5</sub> limits the process only at very small concentrations of BOD<sub>5</sub> [37]. The linear relationship obtained in our study between BOD<sub>5</sub> concentration of leachate and power output allows the MFC system to be used as a BOD<sub>5</sub> sensor as several groups have previously demonstrated [12–15,38].

With regard to the system capability to treat leachate, the low BOD<sub>5</sub> removal obtained is likely to be due to the fact that the flow rates applied were higher than the optimum 48 mL/h. It has already been reported that the fuel removal efficiency can be improved by increasing the retention time [39].

The control column (open circuit C4) showed better removal efficiencies than columns C1 and C2 for COD but not for BOD<sub>5</sub> (data not shown). This suggests that part of the COD removal was not associated with power generation. One reason for this may be the small amounts of oxygen diffusing through the PEM, which is known to be permeable to oxygen [12,40,41]. This would contribute to only a small level of substrate consumption. Substrate could also be utilised through alternative end-terminal electron acceptors, such as sulphate reduction, heterotrophic denitrification, and

methanogenesis [42,43]. Biomass production could also account for additional COD removal [40] and furthermore Rabaey et al. [44] observed that only 20% of the removed COD was actually related to current. Hence, a significant portion of COD in wastewater was probably removed through either alternative electron acceptors or biomass accumulation in the reactors. In principle therefore, the remaining COD should be removed by the anaerobic processes. The COD removal efficiency (calculated as the ratio between the output (treated) levels and influent levels) indicates how much of the available “fuel” had been converted in the MFC, either into electrical current or biomass or through competing reactions with alternative electron acceptors [45].

In terms of removal efficiency of pollutants, column C3 (biological aerated filter) demonstrated better results than the MFC columns. This was probably due to the high volume of support material, which resulted in a higher surface area for biofilm growth, and also to the high rate of mixing as a result of the aeration. This could encourage the loss of a portion of volatile organic compounds (including amines, phenolics and indoles), at alkaline pH values through volatilisation. In addition, it is likely that the MFC columns, which contained the electrode, were working under sub-optimal conditions.

## 5. Conclusions

The MFC system employed in the experiments was able to generate electricity and simultaneously treat landfill leachate with similar BOD<sub>5</sub> removal efficiencies to those produced by a biological aerated filter under similar controlled conditions. Higher flow rates (up to 192 mL/L) improved energy generation in the MFC columns but BOD<sub>5</sub> removal efficiencies required lower flow rates (48 mL/h). The linear relationship obtained between electrical output levels and BOD<sub>5</sub> concentrations allows the MFC system to be used as a BOD<sub>5</sub> sensor. The MFC system described could compete with other conventional biological systems in the treatment of landfill leachate although further work needs to be carried out in order to optimise the configuration and operating conditions.

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