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Treatment of Wastewater in H-Type MFC with Protonic Exchange Membrane: Experimental Study of Organic Carbon and Ammonium Reduction with Electrochemical Characterization

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Food processing industries produce large amount of organic high strength wastewater, thus requiring a treatment before their release in the environment. A serious environmental problem is the ammonium pollution related to nitrogen-rich effluents, such as zootechnical wastewater and anaerobic digestion supernatant. In more recent years, microbial fuel cells (MFC) have been successfully proposed to reduce both pollutants in sludge and wastewater. In this work, the effectiveness of carbon and ammonium removal was investigated in H-type mediator-less MFCs, aiming at evaluating the PEM membrane performances. Anaerobic digestion residue was used as a source of microorganisms. In a first series of tests, synthetic wastewater were prepared by adding sodium acetate or glucose at different ratios, and carbon cycle was investigated. Different ratios, in terms of sodium acetate and glucose (10 gL^{-1}), were tested (100 % v/v Acetate; 50 % v/v Acetate and 50 % v/v Glucose; 75 % v/v Acetate and 25 % v/v Glucose). In the tests devoted to nitrogen cycle investigation, two different ratios in term of initial TOC/NH_4^+ (1 and 0.35, obtained by adding ammonium sulfate) were adopted. During the tests, pH, Total Organic Carbon (TOC), NH_4^+, NO_2^- and NO_3^- concentrations, and Open Circuit Voltage (OCV) were daily monitored. TOC values allowed to assess process kinetic and the optimal experimental conditions for carbon removal. Results showed a carbon reduction up to 78 % in the case of feeding with 75 % v/v Acetate and 25 % v/v Glucose, whilst, in the presence of higher amount of glucose, substrate degradation was found to be affected by pH decrease caused by membrane fouling. In the tests performed to investigate nitrogen cycle, an ammonium reduction to nitrite of 70 % was observed in the cell fed with TOC/NH_4^+ = 0.35 while at TOC/NH_4^+ = 1 the reduction was about 60 %, due to the occurrence of competitive carbon and ammonium degradation reactions. In such a systems, the PEM allowed to assess microaerobic conditions and a good proton transfer ensuring the maintenance of basic pH in the anodic chamber.

1. Introduction

The development of industrial activities continuously produces large amount of wastes: their uncontrolled disposal and release into environment can compromise the natural equilibrium of surface and groundwater (ElMekawy et al., 2015). Therefore, the treatment of wastewater is necessary to accomplish with environmental standards. Specific contaminants are organic carbon and ammonia nitrogen: in particular reactive form of nitrogen in the environment causing a series of side effects; it is responsible, also with sulfur, for acidification, eutrophication and loss of biodiversity of ecosystems (Galloway et al., 2003).
The removal of organic matter from high-strength wastewater is generally performed by biological processes, such as Anaerobic Digestion, AD (Lettinga, 2005). AD is not only efficient for waste management but also for recovery of biogas from organic substrates (Appels et al., 2008). However, this process is vulnerable to chemical compounds like ammonia, NH_3, and ammonium ion, NH_4^+ (Yenigun and Demirel, 2013). The Microbial Fuel Cells (MFCs) represent a technology very promising in the field of Wastewater treatment

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(WWT) (Venkata Mohan et al., 2008). MFCs are electrochemical devices able to convert chemical energy (product by the degradation of organic matter) into electrical energy, using an heterotrophic electrogenic biomass. Although they are not competitive with the AD in carbon reduction, this technologies can be used for the reduction of nitrogen content in wastewater, which is a strong limit for the AD.
Therefore, the goal of this work was to investigate the simultaneous carbon and nitrogen removal in a H-type MFC system, also focusing the attention on the mechanism of nitrogen conversion. To this aim, synthetic wastewater were used, characterized by a different TOC vs. NH_4^+ ratio. Digestate was used as source of microorganism. The objective of a first series of tests was to investigate the effect of different substrate utilization (glucose and sodium acetate) on organic carbon removal in the absence of nitrogen supply (Di Palma et al., 2015), while, in a second series of tests the influence of supplementary nitrogen addition to the anodic solution was evaluated.
Protonic Exchange Membrane (PEM) is an important component of MFCs: it allows protons transfer produced from degradation of organic matter by microorganisms (Zhang et al., 2009), while preventing oxygen diffusion in the anodic chamber.
However, in the view of assessing nitrogen removal from wastewater, a possible solution is to allow the development of reductive pathway in the anodic cell, involving an initial partial ammonia oxidation to nitrite (Ciudad et al., 2005). To this aim, in the present study, a membrane characterized by a oxygen permability was used, to favour the establishment of anoxic conditions in the anodic chamber.

2. Materials and methods

2.1 MFC structure and start-up: inoculum and synthetic wastewater

H –Type MFCs, in pyrex glass and with a volume of 300 ml, were used. The anodic chamber was provided with a reference electrode (Ag/AgCl Crison 5240). The cathodic chamber was open and it was continuously supplied by an air diffuser. Both chambers were equipped by a flat graphite electrode connected by titanium wire. Table 1 shows electrode characteristics. Anodic and cathodic chambers were connected by a CMI Cationic Exchange Membrane (CEM) (Ultrex CMI-7000, Membranes International, USA, ϕ= 53 mm), a gel polystyrene and divinylbenzene cross-link structure containing sulphoric acid groups (Rabaey et al., 2005). with an oxygen diffusion coefficient equal 0.65 10^{-4} cm/s (Kim et al., 2007). So it is strong than the Nafion with different ohmic resistance (Nafion 117- 15 Ωcm^2; CMI 7000- 30 Ωcm^2) (Harnisch et al., 2008).
The cells were joined, hermetically closed, and connected by a titanium wire and a resistance of 180 Ω. The cathodic solution was a buffer phosphate 50 mM, while the anodic solution was a solution of sodium acetate (40 mM) and phosphate (50mM) buffer (Kim et al., 2009). Synthetic feed was a 10 g/l glucose and acetate solution at different ratio (Di Palma et al., 2015). Digestate from the anaerobic digestion of agricultural wastes was used as a microrganisms inoculum (Table 2): 2 ml of digestate were added to the feeding solution to the anodic chamber.

Table 1: Electrode (graphite) characteristics

Density	2.25 g cm^{-3}
Thickness	0.5 mm
Hardness	99.8%
Grains Finishing	Fine
Surface	0.0012 m^2

Table 2: Digestate characteristics

Parameter	Concentration [g L^{-1}]
TSS	30- 40
NH_4^+- N	2
COD	0.006

In the second series of tests performed by adding a 100 mg L^{-1} solution of ammonium sulphate to the synthetic feed, the nitrogen cycle was investigated. The details of the experiments carried out are reported in Table 3.

Table 3: Synthetic wastewater used for removal tests

Run number	Glucose (%v/v)	TOC_{Start}(ppm)	NH_4^+- N (ppm)	TOC/N
T1	50	2450	-	>>1
T2	25	1705	-	>>1
T3	0.08	970	-	>>1
T4	-	2600	100	26
T5	-	100	100	1
T5*	-	2600	2600	1
T6	-	35	100	0.35

The results were compared in terms of ΔOrganic Loading Rate (OLR) defined as

$$\Delta S/\Delta t = (TOC_0 - TOC_f)/\tau \quad (1)$$

where TOC_0 was the initial organic carbon concentration, TOC_f was the initial organic carbon concentration, and τ is the reduction time [day].
The MFC were operated in batch conditions and daily monitored by analysing the anodic solution in term of pH (by using pHmeter GLP21 Crison equipped by an electrode Ag/AgCl), TOC (by using TOC-analyzer Shimadzu), ammonium nitrogen (by using UDK 139- Velp), nitrite and nitrate ions (by using Dionex ICS-1100 Thermo Scientific). Electrochemical analysis, by using a VSP Biologic instrument, including Open Circuit Voltage (OCV) measurement and Linear Sweep Voltammetry (LSV) were performed.

3. Results and discussion

3.1 TOC analysis

The objective of this study was to evaluate the feasibility of MFCs use in wastewater treatment. The results of the experiments are reported in Table 4 where OLRs are shown. The system proved to be effective towards organic matter removal. When comparing the results obtained in tests T1 and T4 (Figure 1), it can be noticed that acetate was more quickly degraded than glucose. In the test T4, just 8 days were enough to achieve a TOC removal rate up to 77%, while the same rate was achieved in test T1 after 17 days. This can be explained by glucose hydrolyzation to acetate that preliminary occurred (Freguia et al., 2008; Chaudhuri and Lovley, 2003). The presence of ammonia nitrogen in T4 not affect TOC reduction because organic content is so high to restrict each type of competition with ammonium-oxidizing microorganisms.
The tests performed in the presence of an additional ammonia nitrogen supply showed a slower TOC removal at lower TOC/N ratio: as a consequence, a longer time to achieve similar removal than in the absence of additional nitrogen was required. Figure 1 shows that TOC degradation followed a first order kinetic in any test, according to the:

$$\ln TOC = \ln TOC_0 - k \cdot t \quad (2)$$

Table 4 summarizes the experimental results and provide the calculated first order coefficents.

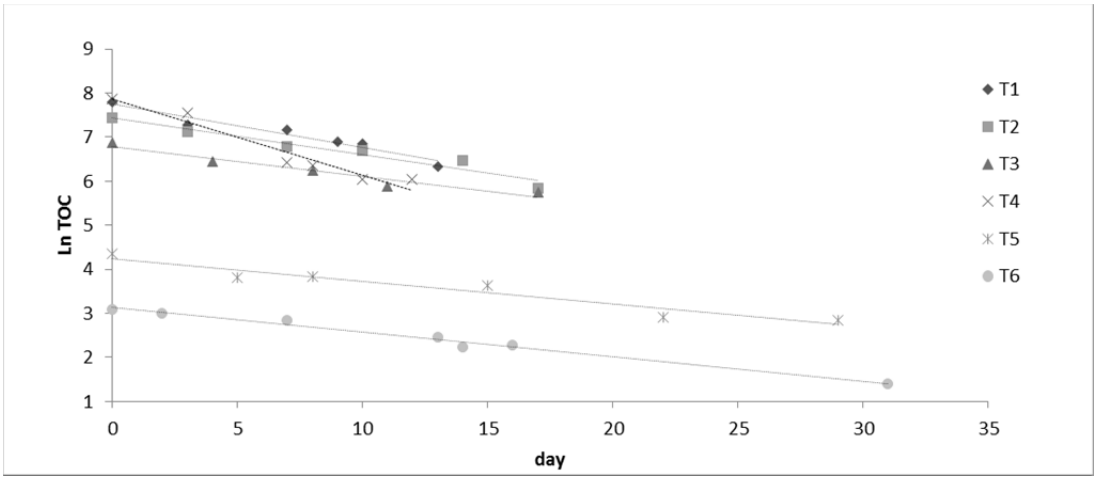

Figure 1: First order kinetic of TOC reduction with and without nitrogen addition.

Table 4: Experimental results and first order coefficents (average) and ΔS/Δt data. Tests were performed in triplicate, and standard deviation is provided.

Run number	$\bar{k}$ (day^{-1})	R^2	Standard Deviation %	ΔTOC(mgL^{-1})	ΔS/Δt (mg l^{-1} day^{-1})
T1	0.0997	0.939	3.13	1884.9	145.00
T2	0.0826	0.940	1.23	1362.1	80.12
T3	0.0677	0.936	1.22	664.0	38.53
T4	0.1725	0.945	1.81	2182.0	181.83
T5	0.0517	0.935	2.45	60.7	2.08
T6	0.0554	0.985	2.12	25.9	0.57

3.2 Ammonium, nitrite and nitrate analysis

Figure 2 and 3 show that in the tests performed with a supplementary nitrogen addition, a substantial nitrite accumulation was observed. The results obtained in T5 and T6 showed a conversion of ammonia nitrogen of 60 ± 3 % and 72 ± 2.8 % respectively, as well as a negligible nitrate concentration, thus confirming the occurrence of a partial nitrification. This behaviour can be addressed to the occurrence of a Shortcut Biological Nitrogen Removal (SBNR), involving first nitrification and then denitrification, according to the following pathway:

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (3)$$

and preventing nitrates formation (Ruiz et al., 2006). By comparing the TOC removal in these tests with the results of the tests performed without any nitrogen supplementary addition, it can be noticed that a high TOC/N ratio determined the inhibition of ammonium-oxidizing microorganism, while at low TOC/N ratio, carbon removal was reduced. As a results of such competition, the time required to achieve an equimolar mixture of ammonium and nitrite in the anodic cells (intersection point of the curves in Figure 2 and Figure 3) was dependant on the TOC/N ratio. According to the results of other studies in literature, such intersection point is important in the view of starting a second step of N-cycle like Anammox process (Tsushima et al., 2007; Li et al., 2015; Ma et al., 2015).

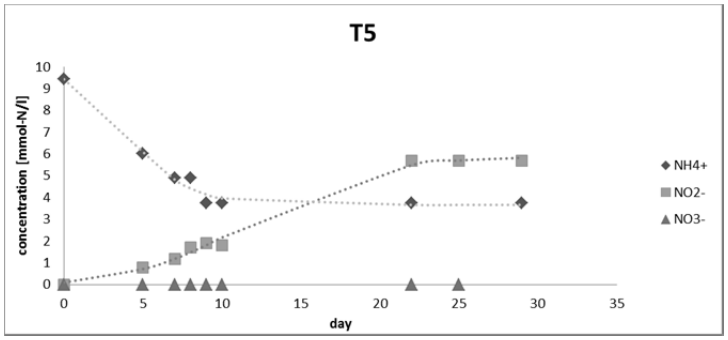

Figure 2: Ammonium reduction and nitrite accumulation at TOC/N= 1.

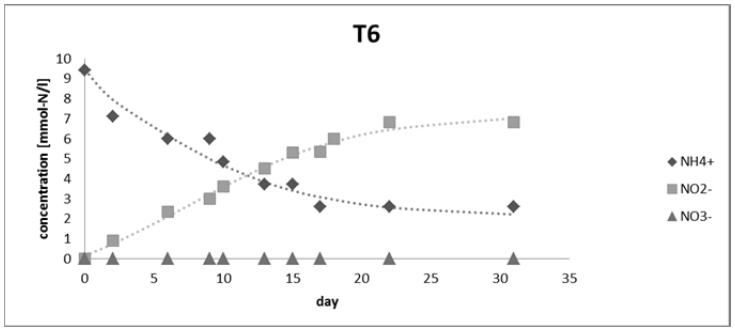

Figure 3: Ammonium reduction and nitrite accumulation at TOC/N= 0.35.

3.3 Electrochemical characterization: OCV and LSV

Electrochemical analysis results show that the presence of nitrogen did not interfere with the mechanism of electrons exchange (Figure 4). A particular trend was observed in T1 where steady conditions were not attained, but, after an initial increase, an OCV decrease was measured.

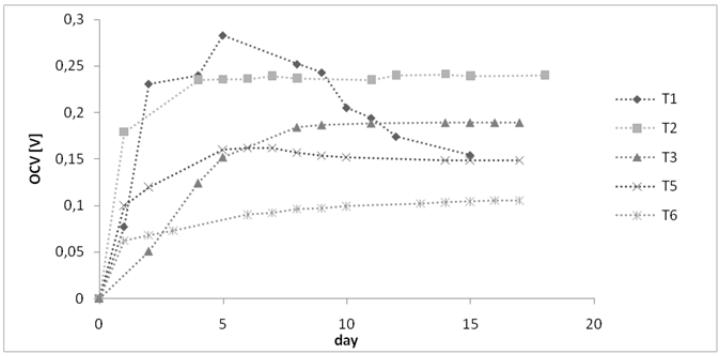

Figure 4: OCV daily analysis and influence of glucose concentration.

This specific behaviour can be explained considering the pH evolution trend in the anodic cell during test T1. In fact, as shown in Figure 5, in such test, due to the high glucose concentration, a strong pH decrease was observed as a result of the above mentioned glucose hydrolysis. Conversely, in the presence of a lower amount of glucose (25 v/v % as in test T2), the H^+ production was neutralised by phosphate buffer: a lower initial pH reduction was observed, and pH attained almost neutral value. On the contrary, in the tests T3, T5 and T6, where small or negligible amount of glucose were fed, the presence of buffer phosphate ensured negligible pH fluctuations. This imply that a maximum glucose concentration in the cell can be adopted, to prevent system outage due to the establishment of acidic conditions.

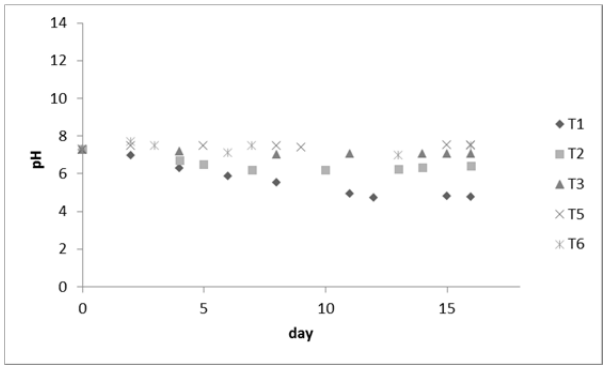

Figure 5: pH values and influence of glucose concentration.

Polarization curves obtained by LSV technique in tests T4 and T5* are reported in Figure 6. The difference in initial nitrogen content, slightly affected cells performances: the measured overall cells internal resistance was 300 Ω and 366 Ω in the absence or in the presence of nitrogen, respectively (Fan et al., 2008; Di Domenico et al., 2015).

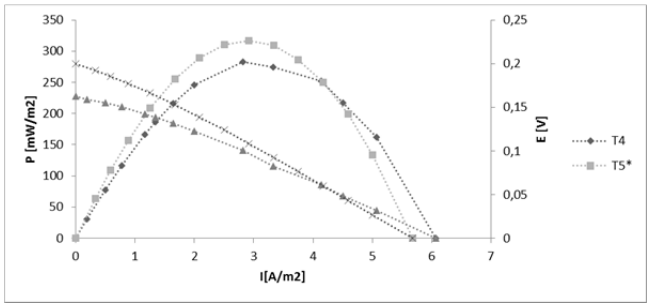

Figure 6: Polarization curves.

4. Conclusion

The goal of this study was the evaluation of the performances of an H-type MFC in term of organic carbon and ammonium nitrogen removal. Synthetic wastewaters, with different TOC/N ratios, were tested, using anaerobic digestate as a bacterial source. Carbon reduction (up to 78 %) resulted to be enhanced by values of TOC vs. N ratio higher than 1, while a high ammonium reduction (up to 70 %) was obtained when the TOC vs. N ratio was lower than 1. In the latter case, the cation exchange membrane supported nitrite accumulation, that is the first step of ammonium conversion into molecular nitrogen (N_2), by ensuring the optimal value of OD in anodic chamber. As regards the electrochemical performances of the system, a high ammonium content in the media determined an increase of the cell internal resistance.

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