

A semi-pilot microbial electrolysis cell (MEC) for hydrogen production and pig-slurry valorization.

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Current situation of farm wastes

The amounts of slurry and manure produced each year are steadily rising as a result of an increasing demand for livestock products, which are expected to almost double by 2050 [1]. This two byproducts of farm-activity are commonly used as a fertilizer for crops production. However, their direct disposal may also overcome soils capacity to absorb nutrients in some areas [2], thus giving to rise to health and environmental issues. This demands the use of feasible and efficient waste management technologies that help to limit the impact of these wastes.

MEC: a novel technology for wastes valorization

Bioelectrochemical systems (BESs) represent an emerging technology whose principle of operation is based on conventional electrochemical systems in which at least one of the electrode reactions (anodic and/or cathodic) are biologically catalyzed. From a practical point of view -as with many other electrochemical systems- BES can be used to produce electrical energy, in which case they are referred to as microbial fuel cells (MFCs), or can be used to produce valuable chemicals (by providing a certain electrical energy input to the BES), in which case they are referred to as microbial electrolysis cells (MECs). For a more detailed information on BES the reader is referred to [3].

MEC technology hold a great potential for practical applicability, as they allow for energy recovery from organic waste streams. In brief, if a biodegradable organic waste is fed to anode of a MEC, it is possible to oxidize (mineralize) the organic matter and use the electrons collected on the anode to produce hydrogen on the cathode with the help of an external power source.

Our approach



Figure 1. Laboratory set-up.

In this study we aim to characterize the performance of two semi-pilot MECs (each having a total volume of 16L) designed for pig slurry valorization (Figure 1). We pay special attention to hydrogen production rates, organic matter degradation rates and energy consumption. In addition, and as pig slurry contains considerable amounts of ammonia (NH_4^+), we make use of the charge transport phenomena within the electrolytes to recover this valuable chemical (NH_4^+ is used mainly as a feedstock by the fertilizer industry) on the catholyte. This would allow to improve the economic feasibility of the proposed technology.

Material and methods

The MECs consist of 4 methacrylate plates arranged in parallel with a rubber sheet between each plate (Figure 1). The two side plates act as walls of the reactor, while the central plates have been emptied and act either as anodic or cathodic chambers. The anodes are made of 5 mm-thick graphite felt, while the cathodes are made of a stainless steel mesh. Both electrodes had a projected surface area of 2226 cm^2 and were wired to a power source (applied voltage of 1V between anode and cathode) through titanium wires. The anolyte consisted of the pig slurry being treated (Table 1) while the catholyte consisted of a phosphate buffer (PBS 0.1 M) and they were separated by means of a cationic exchange membrane (CEM) to allow the NH_4^+ cations to flow from the anolyte to the catholyte.

Parameter	Units	Value
COT	g/L	2,81
Acetate	mg/L	173
NT	g/L	2,03
Phosphate	mg/L	32
Sulphate	mg/L	34
chloride	g/L	2,06
TSS	g/kg	17.3
VSS	g/kg	7.6
% VSS	%	44
pH	-	8
Conductivity	mS/cm	20.4

Table 1. Pig slurry characterization.

Results and discussion

The anodes of the MECs were inoculated with a mixture of sewage sludge and the effluent of the anodes of MECs previously operated in our laboratory, amended with acetate (200 mg L^{-1}). Following the inoculation, the electrical current started to gradually increase (there was a lag phase of $\sim 24\text{h}$) and stabilized after a period of 16 days at a current density of 3.5 A per m^2 of anode. Once current stabilized the reactors were operated in batch mode (retention time was fixed at 24h according to previous results obtained in our laboratory). The anode was initially fed with 20% diluted pig slurry, and the dilution rate was gradually increased to favor the acclimation of microbial communities to this complex substrate.

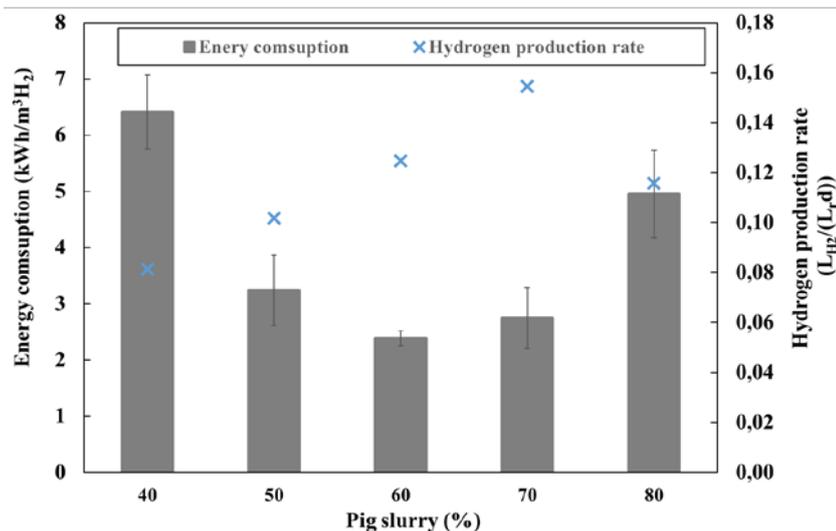


Figure 2. Energy consumption and hydrogen production rate as a function of the amount of pig slurry in the feed.

Hydrogen production rate tended to increase by increasing the amount of pig slurry in the feed, reaching a maximum of 0.16 L of hydrogen per liter of reactor and per day ($0.16 \text{ L}_{\text{H}_2} / (\text{L}_R \text{ d})$) at a dilution rate of 70% (Figure 2). Interestingly energy consumption also improved with the dilution rate, reaching a minimum of ~ 3 kWh per m³ of hydrogen ($3 \text{ kWh}/(\text{m}^3\text{H}_2)$) which is with the range of the energy usage made by conventional hydrogen producing technologies [4]. When the amount of pig slurry in the feed was increased to 80%, both hydrogen production and energy consumption were penalized, probably as a result of organic overloading or ammonia inhibition. Therefore, the optimal dilution rate seems to be in the range 60-70%.

As mentioned before, the MECs were provided with a cationic exchange membrane to allow for recovering part of the NH_4^+ present in the pig-slurry. Maximum NH_4^+ recovery efficiency reached 57 %, which corresponded to a recovery rate of $325 \text{ mg-NH}_4^+ (\text{L}_R \cdot \text{d})$.

Organic matter removal efficiency was quite limited (always below 20%) due to the low biodegradability of pig slurry. This in turn has a negative impact on hydrogen production and ammonia recovery rates as they are proportional to organic matter degradation on the anode. Thus we hypothesize that the overall efficiency of the process could be improved by increasing the amount of biodegradable matter in the feed. This could be done by diluting the pig slurry in an easily degradable carbon-rich waste such as cheese whey. This approach would help to exploit interesting synergies in the management of different wastes that are being produced by agroindustries.

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References

- [1] ten Hoeve M, Gómez-Muñoz B, Jensen LS, Bruun S. *J Environ Manage.* **181** (2016) 710–720.
- [2] Santos A, Bustamante MA, Tortosa G, Moral R, Bernal MP. *J Clean Prod.* **112** (2017) 81–90.
- [3] Escapa A, Mateos R, Martínez EJ, Blanes J. *Renew Sustain Energy Rev.* **55** (2016) 942–956.
- [4] Conte M, Di Mario F, Iacobazzi A, Mattucci A, Moreno A, Ronchetti M. *Energies.* **2** (2009) 150–179.