Dissolved CO_2 valorization by means of microbial electrolysis cell (MES) using anaerobic sludge from an agricultural digestate

M. Menini, G. Pesante, J.E. Rodriguez Gamero, D. Bolzonella, N. Frison

Department of Biotechnology, University of Verona, Verona, 37134, Italy
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Presenting author email: miriam.menini@univr.it

Carbon dioxide (CO_2) is a gas that is naturally available in the atmosphere. Due to the world's population growth and the consequent increase of energy demand, the amounts released by human activities have increased and CO_2 has therefore become one of the major contributors to the greenhouse effect. In fact, every year nearly 35.5 gigatonnes (Gt) of anthropogenic CO_2 are emitted in the atmosphere, which is believed to be the main cause of climate change (Mac Dowell *et al*, 2017; Mohan *et al*, 2016). This increase has led to a global interest for eco-friendly technologies which can help meet our energy demand without the production of CO_2, or that can sequester the CO_2 already found in the atmosphere. The fixation of CO_2 is made by plants, microalgae and some microorganisms, and some recently developed technologies can utilize these CO_2 fixing organisms for the concomitant production of electricity, for example bioelectrochemical systems (Mohanakrishna *et al*,2016).

Bioelectrochemical system (BES) is a technology developed to produce energy from wastewater, but it has become of wider use in processes such as resource recovery, bioremediation and water desalination. In particularl, the production of value-added products and concomitant capture of CO_2 by means of microbial electrosynthesis cells (MESs) is now becoming a promising field of study. MES technology works by providing an electrical voltage to the cell in order to perform a non-spontaneous reaction, the CO_2 sequestration, to produce added-value compounds (e.g., acetic acid, biofuel, hydrogen) (Bajaracharya, 2016).

In this context our study evaluates the use of a mixed microbial community to fix CO_2 using an applied voltage taken from the alkalinity available from the anaerobic digestate of agricultural residues. The major aim of this work is the conversion of CO_2 into valuable organic material, such as the Volatile Fatty Acids, (VFAs) as bio-based building blocks. A two-chambers (H-type) MES was set up, with anaerobic sludge taken from a full-scale anaerobic digestion reactor treating organic waste at the cathodic chamber, while the anodic chamber was filled with tap water and kept under abiotic conditions. The source of inorganic carbon was taken directly from the dissolved CO_2 already available in the anaerobic supernatant. The H-cell was made of two glass bottles (each with a total volume of 1000 mL) representing the anodic and cathodic compartments. The chambers were separated by a proton exchange membrane (PEM), specifically a Nafion® 117. This membrane was previously treated as specified in Paiano *et al* (2019). As for the electrodes, graphite rods were the working and counter electrodes representing the cathodic and anodic chambers respectively;a KCl saturated Ag/AgCl (+199 mV vs. the Standard Hydrogen Electrode, SHE) was also placed in the cathode compartment as reference electrode. The graphite rods were equipped with titanium wires which allowed the connection between the electrodes and the potentiostat (Ametek, Berwyn, Pennsylvania, USA) for the electrochemical measurement. The experiment lasted 36 days and a sample was taken daily from both the control (open circuit, no voltage applied) and the test (applied voltage, -0.7V vs SHE). During the experimental period, the current was monitored by means of a potentiostat.

The characterisation of the substrate was made according to the standard methods (APHA, AWWA, WEF, 2007) and is reported in Table 1.

Table 1. Characteristic of the anaerobic digestate (COD= chemical oxygen demand, TS= total solid, TVS= total volatile solid, ww= wet weight)

Characteristic	Unit	Anaerobic digestate
Total solids	gTS/kg(ww)	36,1
Volatile solids	gTVS/kg(ww)	22,3
Total COD	gCOD/L	22,5
Ammonia	mgN-NH_4/L	3150
Alkalinity	mg$CaCO_3$/L	24423
pH	-	9.9

As it can be seen in Figure 1, at the beginning of the experiment the current at was -3.87 mA, and it increased during the experiment until it stabilized at -1.43 mA around day 13. The same stability was achieved for the soluble COD (sCOD) at day 11, which was 31.2 gCOD/L in the cathodic chamber and 26.9 gCOD/Lfor the control (Figure 2). The alkalinity during the experimental period slowly decreased in the applied voltage test, while it remained stable in the open circuit test (control) (22970 and 23793 mg$CaCO_3$/L respectively). The maximum VFAs production was obtained on day 7 and was 1.1 gCOD/L at the cathode and 1.2 gCOD/L in the open circuit test, with acetic acid found to be the most aboundant in both the tests. In both chambers there was no passage of VFAs through the PEM, but the pH dropped below 5 after 6 days of performance in the applied circuit test.

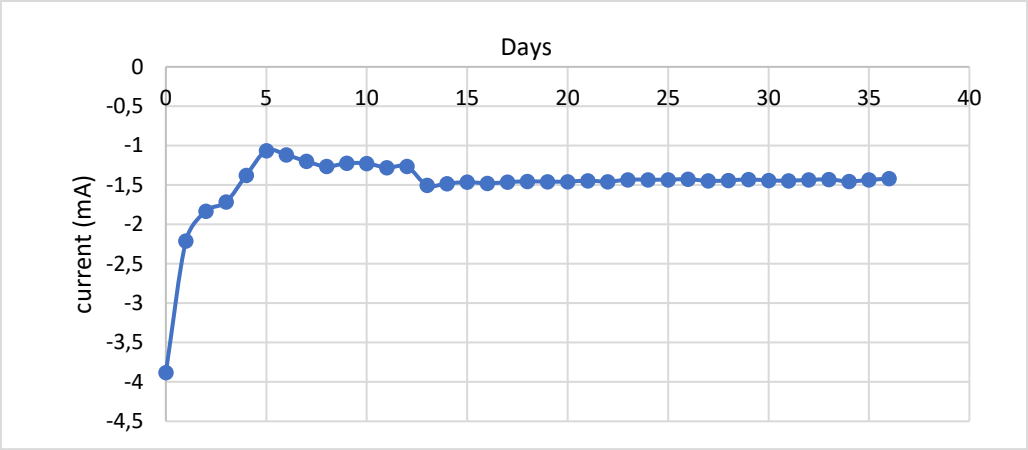

Figure 1. Test's current trend during the experimental period expressed in mA.

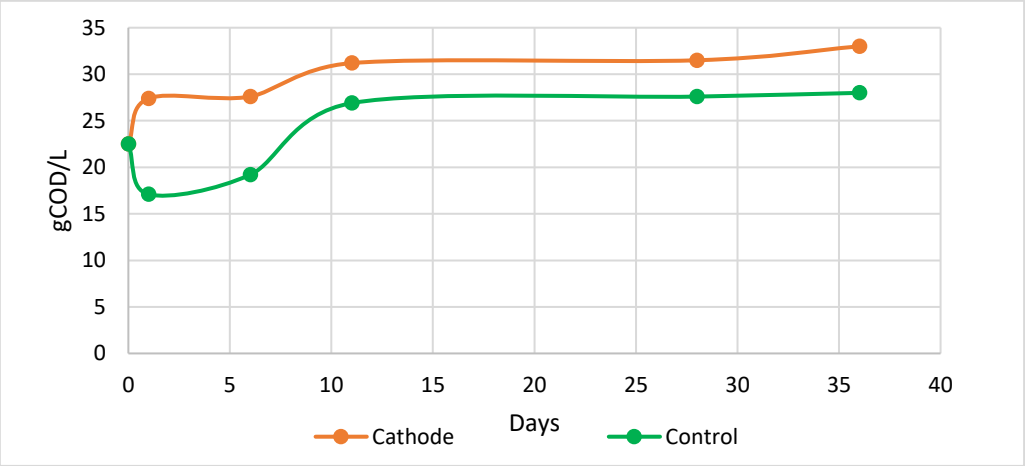

Figure 2. Soluble COD (sCOD) trend during the experimental period.

In conclusion, the decrease of alkalinity in the applied voltage test and the subsequent increase of soluble COD could be the result of the current stabilization after 11 days. These results suggest that part of the CO_2, expressed in terms of alkalinity, is fixed and turned into volatile fatty acids (particularly acetic acid). More investigations are required to confirm this initial results.

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