Influence of ions accumulation on hydrogen production from Organic Fraction of Municipal Solid Waste (OFMSW)

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Municipal solid waste is one of the most suitable resources to produce high value molecules through biological processes. Among them, the organic fraction of municipal solid waste (OFMSW) has a high calorific value due to the high content of volatile solids (VS) making it suitable for bioenergy production (Alibardi and Cossu 2014). By coupling fermentative hydrogen production with an anaerobic digestion process, a mixture of H2/CH4 (5-20%) so called Hythane®, as a new type of efficient biofuel, can be generated. By separating hydrolysis/acidogenesis and methanogenesis, each reactor can be optimized for improving the overall energy recovery with regards to a traditional one-step AD process (Blonskaja *et al* 2003).

The proposed concept consists in a first dark fermentation step, where hydrogen and other microbial metabolic compounds such as volatile fatty acids (VFA) are produced from household solid waste. The most recalcitrant but still biodegradable solid substrates and the VFA that accumulated in the fermentation bulk phase (such as acetate, butyrate and propionate) are converted into methane in a second stage. Overall, a maximum of organic matter is transformed into valuable and easily extractable products, ie biogases. The liquid phase, so-called leachate, can also be recirculated into the first reactor for microbial inoculation. In such configuration, a thermal pretreatment is required to avoid further growth of H2-consuming methanogens. However, after several cycles, various ions that are naturally present in municipal solid waste, can accumulate and cause microbial inhibition, in particular on hydrogen-producing bacteria (HPB). Indeed, the hydrogen producing pathways are limited by the accumulation of ions such as chloride of ammonia nitrogen (Cavinato *et al* 2012; Pierra *et al* 2013). Moreover, it was already reported that an accumulation of ions increase the osmolarity and leading to an inhibition of microbial activity (Walter *et al* 1987).

The objective of this study was therefore to investigate the impact of ions accumulation on hydrogen-production microbial pathways.

Ions were added and selected according to their natural occurrence in leachates of municipal solid waste, and the ionic strength was used as indicator of global concentration. During the experiments, the ionic strength concentration ranged from 0.09 to 3.0 mol/L using different solutions of ions (different sets of cations (NH4+, Ca2+, K+, Na+, Li+, Mn2+, Mg2+) and anions (Cl-, PO42-, SO42-, Br-)). The fermentation experiments were carried out at 37°C, pH 6 using a freshly prepared synthetic Organic Fraction of Municipal Solid Waste (OFMSW). The substrate representing the average composition of OFMSW collected in France which was composed of paper, cardboard and food waste. All the experiments were carried out in a 500 ml bottle with 400 ml total medium volume. The total volatile solids (VS) amount of the fermentation medium was 9.25 gVS with a S/X (OFMSW substrate/microbial biomass on VS basis) ratio of 20. The gas composition was measured using gas chromatograph Perkin Clarus 580. In total, 152 batch reactors were operated with five ions solutions at different concentrations.

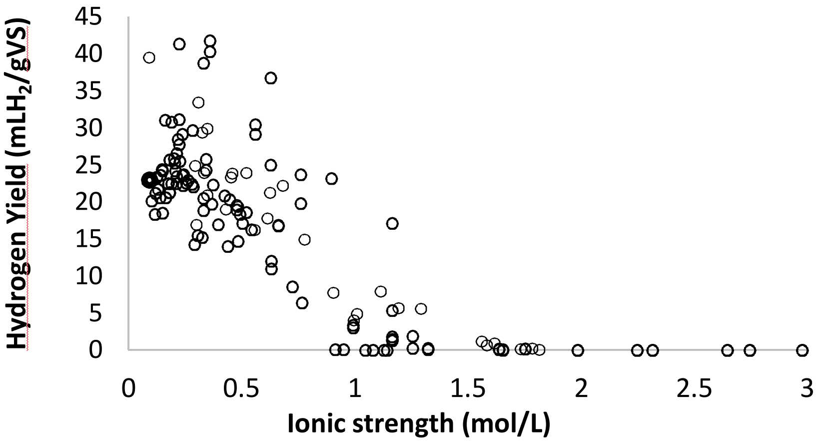

Figure 1 : Effect of ionic strength on biohydrogen production in dark fermentation batch reactor

Hydrogen yields are presented in Figure 1. At low ionic concentrations (from 0.09 to 0.7 mol/L), the results show a slight positive effect on the hydrogen production with an average yield of 23.2±6.5 mLH2/gVS. Such observation confirms the benefice of adding certain ions, for instance ammonia nitrogen or phosphate, on microbial activity as already described in the literature (Wang and Wan 2009). Moreover, this result is consistent with the study of Favaro *et al* (2013) using the same operational conditions (37°C, pH: 7, heat treatment and FFOM) who reported a H2 yield of 23.4±2.9 mLH2/gVS.

However, at higher concentrations of ions (from 0.7 to 1.2 mol/L), a strong variability of hydrogen yield with a global decrease of the performances (5.9±7.3 mLH2/gVS) was observed whatever the couple of ions considered. Interestingly, ionic inhibition started around a similar threshold value of ionic strength (0.75±0.13 M) for all types of ions. A total inhibition of hydrogen production was observed beyond an ionic strength of 1.2 mol/L. These results suggest that a global inhibition may be responsible of the negative impact on hydrogen production and not a specific molecule. The VFAs production followed a same trend, by reaching a total inhibition of the fermentative activity at high ionic strength (data not shown). Finally, microbial characterization analyses showed that ions accumulation leads to a modification of microbial community with the development of non-hydrogen producing bacteria as *Marinocpirillum minutulum* and *Atopostipes suicloacalis* which are known to be resistant to halophilic conditions. As already described by Van Niel *et al* (2003), the negative impact of the ionic strength on hydrogen producer bacteria can be due to a cell lysis which could be caused by activation of autolysins.

In conclusion, these results showed a strong inhibitory effect of ions on dark fermentation. Whatever the type of ions considered, a similar inhibition threshold value of the ionic strength was observed around 0.75±0.13 M. In a context of dark fermentation upscaling and prior to implement this technology in waste treatment plants, ions accumulation in leachate recycling should be carefully monitored to avoid lower process performances by reaching a critical threshold in terms of ionic strength.

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