CO_2 utilization in a system of solid metal waste and anaerobic granular sludge for acetic acid production based in a circular economy concept

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Introduction

Substantial research interest has been focused over the past decades to human activities that affect negatively the climate system, specifically focusing to the greenhouse gas emissions and to the efforts for the mitigation of the carbon dioxide (CO_2). It is observed that energy demands are increased dramatically every year leading to the excessive use of fossil fuels whose combustion has as a consequence of the increasing of CO_2 to the atmosphere resulting to global warming. It is estimated that the human activities constitute about 25 to 35 gigatonnes of CO_2 released to the environment annually (Ruiz-Valencia *et al* 2019). Furthermore, it is observed that the global resources are over exploited and slower renewed (Child *et al* 2018). Hence, EU concerning about the notable negative effects to the climate due to the greenhouse gasses emmisions promotes policies for the emissions reduction and defines action programs such as "Europe 2020". Following these efforts, on the 12th of December 2015 has been signed the Paris agreement and EU has been committed for gas emissions reduction of 40% below 1990 levels until 2030, and introduces new definitions such as "circular economy", "waste to energy", "zero waste" etc. aiming to achieve these goals. Thus, researchers and engineers examined several strategies ranging from forestation to innovative technologies for the transformation of carbon dioxide into platform chemicals and fuels – also known as carbon capture and utilization (Prévoteau *et al* 2020).

Although, CO_2 constitutes the main greenhouse gas leading to the global warming (Yang *et al* 2017) and the ocean acidification (Hönisch *et al* 2012), it has been proposed as a safe, economical and renewable carbon source (Saeidi *et a*l 2014). It has been also characterized as an environmental friendly chemical reagent (Sakakura *et al* 2007). However, the existing technologies for mitigation of CO_2 demand high energy consumption due to CO_2 presents kinetic and thermodynamic stability because of the centrosymmetric structure (O=C=O) (Hu *et al* 2013) and the use of high energy substances such as hydrogen, are required for utilization (Omae, 2006).

In this work, we proposed the CO_2 conversion to acetic acid in a system of zero valent metal and anaerobic sludge. Specifically, the H_2 can be generated by zero valent metal (fig.1, eq.1) and can be utilized to acetic acid by homoacetogens (fig.1, eq.3). However, the same substrate (H_2 and CO_2) can be utilized by hydrogenotrophic methanogens to CH_4 as shown at fig.1 (eq.2) and can act antagonistically with homoacetogens. Interestingly, Vyrides *et al* (2018) pointed out that hydrogenotrophic methanogens suppress homoacetogens in this system. Apart from this, CH_4 can also be generated by acetoclastic methanogens according to eq. 4 (fig. 1). Based on the above concept, the purpose of this study was to examine a new approach for bioconversion of CO_2 (as a sole carbon source) to acetic acid using anaerobic granular sludge and metals such as zero valent iron, magnesium and waste iron scrub. To achieve this, methanogens were inhibited using 2-bromoethanesulfonate (BES) and therefore homoacetogens were enriched in an environment with high CO_2 and H_2 as shown at fig. 1

Material and methods

The bioconversion is carried out using anaerobic granular sludge (80 gr/L), a dynamic system of bacteria consortium, in the presence of magnesium or ZVI (waste iron scrub will be examined) that through the anaerobic oxidation produce abiotic hydrogen. The enrichment of the acetogens in our system that produce the above mentioned VFAs is achieved under mild conditions (pH: 6.5-7 and 33C°) through the inhibition of methanogens that act antagonistically and takes away significant portion of reactants (acetate and hydrogen). For the inhibition of methanogenesis and increasing the production of acetic acid, different strategies were implemented without the need of sterilization or high cost chemicals and pretreatment steps blocking specific reactions (eq.2 and eq.4) as shown in the fig. 1. To assess the potential inhibition of methanogenesis procedure and homoecetogens enrichment in an anaerobic granular sludge system a) 2-bromoethanesulfonate (BES) chemical at low consecration (4mM), b) short exposure of anaerobic granular sludge to heat c) exposure of anaerobic granular sludge to salinity 50 gNaCl/L - 90gNaCl/L were investigated in the presence of strip metal of magnesium (4 gr/L) that react constantly with water and produced hydrogen. The bacteria community that existed in the batch experiments will be identified analyzing the 16s rRNA after the DNA extraction. Furthermore, structural characterization of the metals or waste metals at the end of the experiments will be examined performing X-ray diffraction analysis.

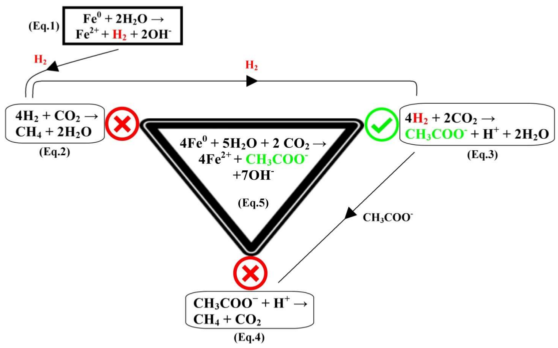

Figure 1: Chemical reactions that take place during the CO_2 utilization

Results and discussion

Preliminary results presented demonstrated that methanogenesis procedure can be effective inhibited using sodium chloride and the highest performance observed (500 mg/L and 470 mg/L of acetic acid) when anaerobic granular sludge was exposed to 50 gr/L and 70 gr/L of sodium chloride respectively. Increasing the salinity to 90 gr/L resulted the fully inhibition of methane but the acetic acid produced in a lower concentrations (280 mg/L) (fig. 2). Mg was fully dissolved producing significant amounts of hydrogen that consumed by homoacetogens.

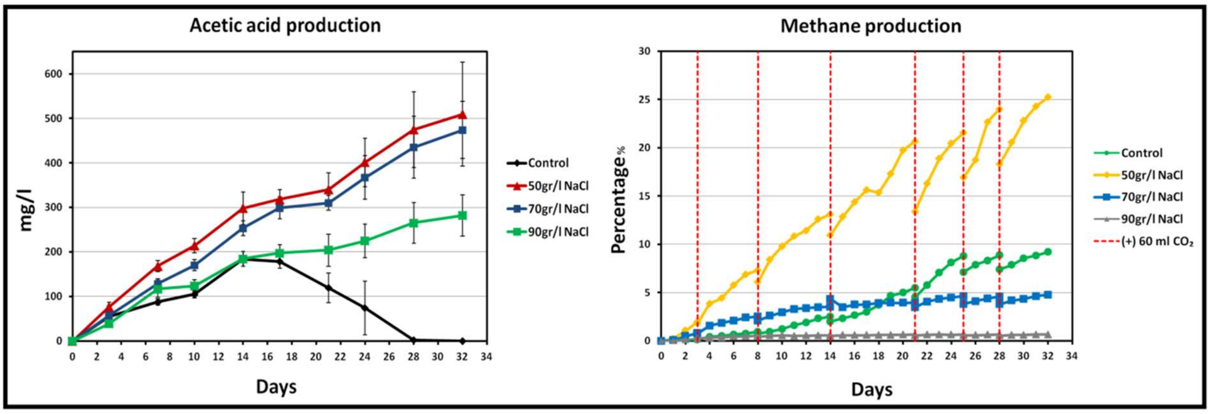

Figure 2: Methane inhibition using different concentrations of sodium chloride and acetic acid production.

Conclusions

This study has shown a new approach for CO_2 conversion to acetic acid based on the use of anaerobic granular sludge and metals or/and waste metals under aquatic mild conditions. High salinity, BES and thermal methane inhibition were investigated in an attempt to develop an innovating technology which mitigates climate change and reduces greenhouse gas emissions using waste metals for the production of abiotic hydrogen that is required for the metabolic reactions of bacteria. The technology proposed was effective in VFAs production and can be contribute execute the goals that set up by EU under the framework of circular economy and waste valorization. The process could be further enhanced through optimization of different parameters in a pilot scale.

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