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Microbial Electrolysis Cell II

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1. Abstract

The production of methane in pilot scale microbial electrolysis cell (MEC) installations was investigated to examine the potential implementation of large-scale MEC-technologies into wastewater treatment plants (WWTPs). The purpose of this project was to produce biogas from WWTPs sewage sludge at room temperature and high purity methane in order to lower wastewater cleaning costs. MEC technology can reduce the energy consumption and the amount of residual sludge waste in comparison to traditional biological treatments while generating and storing energy. For this purpose, two different types of reactors were developed to assess the process feasibility in terms of biogas production and quality.

The horizontal bioelectrochemical reactor with a volumetric capacity of 50 liters, is composed by 16 reticulated vitreous carbon (RVC) based anodes and 15 nickel cathodes. At room temperature, under anaerobic, semi-batch conditions and potentiostatic application (E = 1.0 V), about 40 liters of biogas were produced in 40 days of application. A maximum methane fraction of 90%mol can be achieved in certain experiment by using digested sludge from the Châteauneuf's WWTP. The reactor was operated continuously in single-pass mode with a sewage sludge flowrate of 5 ml/min. Almost 140 liters were produced in 1000 hours of microbial electrolysis with a methane fraction in the biogas produced that reached a maximum concentration of 79%mol and the minimum during the continuous MEC process was of 73%mol. The inlet soluble COD of the sewage sludge was measured to be 2324 mg/l and the outlet COD was of 145.6 corresponding to a COD reduction of 93.7%.

A methodology was established to characterize the methane production under continuous potentiostatic application and sewage sludge circulation. For that purpose, pulses at determined applied voltages and no potential application at open circuit were realized and the volumes of methane produced were assessed. At 2.5 V a maximum current efficiency of 100% for the direct carbon dioxide reduction into methane has been reached during a pulse of 7 hours. An enhancement factor of 1.23 was calculated in this experiment suggesting a possible catalytic activation of the methanization through the potential application. This phenomenon was clarified by increasing the pulsing time since the methane production was enhanced (i.e. >1) at the beginning of the pulse and the overall pulse current efficiency was calculated to be 83.3 %.

The second MEC technology based bioelectrochemical system is a column reactor and has also a volumetric capacity of 50 liters. The Column-MEC (usable as Trickle Bed Reactor, TBR) is composed by three electrochemical drawers, each one made of 10 RVC anodes and 10 RVC cathodes. At room temperature, under anaerobic, semi-batch conditions and potentiostatic application (E = 0.6 V), it has been possible to produce 23 liters of biogas within 420 hours of application (i.e. 17.5 days) with a maximum methane fraction of 99 %mol, by using mixed sludge from the Châteauneuf's WWTP.

The metagenomic data analysis of the biofilm at the electrodes' surfaces has demonstrated that the majority of the microorganisms are bacteria which are involved in the organic matter degradation and syntrophic reactions leading to acetate and CO_2. The archaea identified were all related to the methanization since their metabolism uses hydrogen, carbon dioxide and acetate to produce methane.

In this study, it was demonstrated that MEC technology can produce at room temperature high volumes of biogas containing 10-30 %mol more CH_4 than the biogas produced at 37 °C in the anaerobic digesters at the Châteauneuf's WWTP. Moreover, the MEC process is achievable at minimum energy consumptions of 3.06 $J/ml_{methane}$ which is about 13 times lower compared with methane's energy of combustion (i.e. 39.7 $J/ml_{methane}$).

2. Introduction

Wastewater treatment (WWT) represents nowadays a crucial industrial, environmental, and economic technology. Traditional WWT processes are in constant evolution and challenged by the demand in renewable sources of energy (Villano et al., 2010). In this context, anaerobic digesters (AD) allow to recover energy from organic wastes by producing biogas which contains methane (CH_4), an energy-rich product, from biofermentation (Sakaki et al., 2011). However, the conventional AD processes are limited in terms of process efficiency and sustainability. Moreover, the management of large volumes of primary and activated sludges implies important operational and energy costs in wastewater treatment plants (WWTP).

Bioelectrochemical systems (BES) are being developed and investigated to enhance energy recovery from WWT. Although most of the interest has been focused on the development of Microbial Fuel Cell (MFC) which generates electrical energy from the biocatalyzed anodic oxidation of organic matter, the attention has recently shifted towards microbial reductive processes and in particular on the carbon dioxide (CO_2) reduction into CH_4 (Rosenbaum et al., 2014).

Microbial electrolysis cell (MEC) is a BES that can be used to produce biogas such as hydrogen (H_2) and methane (CH_4) from organic wastes through cathodic reactions. The term electromethanogenesis was used to refer to an alternative methanogenic pathway described (Cheng et al. 2009) for the first time, where CO_2 is reduced by a single archaeon (i.e. *Methanobacterium palustre*) using electrical current supplied to the reactor. Methane production in a biocathode at a cathodic potential lower than 0.5 V vs. SHE, with 96% of the applied current converted into methane at poised potential of 1.0 V vs. SHE was observed and the fact that methane was directly produced from current rather than hydrogen was suggested for the first time.

Therefore, this BES has a good potential to become an alternative to the conventional anaerobic digestors (AD) as, it operates at lower temperature, it could produce upgraded biogas or even pure gases and it reduces the residual organic wastes (Zeppilli et al., 2015, Sugnaux et al., 2017). Although most of the early studies with MEC technology focused on H_2 production, methane-producing MECs received more attention these past 10 years (Blasco-Gómez et al. 2017). This new interest is due to their simplicity in term of design (i.e. membraneless MEC), an easier gas storage management (Escapa et al,. 2016), a potential for direct CO_2 fixation (Zhang et al., 2019) and better quality of biogas (i.e. less CO_2).

The main goal of this study is to enhance biogas production at lower energy consumptions compared to conventional AD processes and to produce high quality biogas (high CH_4: low CO_2 ratio) and even almost pure biomethane (i.e. > 95% mol CH_4) with novel MEC reactors designs.

Two different reactors designs based on MEC technology are explored in terms of methane production and purity. Moreover, the influence of key parameters such as the applied potential and the substrate (i.e. WWTP sewage sludge) are investigated in order to understand their impact on the biomediated methane electrosynthesis. The contributions of biofermentation and Faradaic reaction have been analyzed and the results were compared with the results reported on literature and with the biogas production at Châteauneuf's STEP using conventional AD process, in terms of methane quality, process efficiencies and energy consumption.

2.1. Microbial Electrolysis Cell (MEC)

A microbial electrolysis cell reactor is designed as a microbial fuel cell (MFC) with the anode(s) connected to the cathode(s) by an external electric circuit and with the organic wastes as electrolyte. The main difference between MEC and MFC is that an additional voltage is applied by a power supply to promote reactions in the reactor, while MFC generate electricity as an output.

Anaerobic microorganisms are key-elements for the functioning of a methane-producing MEC. Two types of microbial communities should be present for an optimal operation: (i) a microbial biofilm community on the anode that oxidizes acetate from organic wastes into CO_2, protons, and electrons. This microbial community is described as “electrogenic” because the microorganisms can transfer the electrons from their catabolism to solid electrons acceptors to gain energy (e.g. anode) (ii) a second microbial community that uses these generated products of the organic matter oxidation (CO_2 and H_2 or electrons and protons) to metabolize the targeted methane. These microorganisms are known as hydrogenotrophic methanogens.

As mentioned above, a small voltage applied between the anode(s) and the cathode(s) by a power supply can promote methanogenesis. This applied potential is expected to help the implantation and the maintenance of specific microbial methanogenic communities at the cathode(s) and promote specific cathodic reactions.

Two metabolic pathways were proposed to occur at the cathode (Equation 1, Equation 2, Sugnaux et al., 2017).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
Equation 1

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$
Equation 2

In the first equation, methanogenic microorganisms reduce molecular H_2 generated at the cathode through hydrogen evolution reaction (HER). HER is an electrochemical process occurring at the interface between the cathode and the electrolyte. This pathway (Equation 1) is known as mediated electromethanogenesis. In the second equation, methanogenic microorganisms use the supplied electrons from the cathode in addition to the protons present in the sludge (H^+) (Cheng et al., 2009; Villano, M. et al. 2010). This pathway (Equation 2) is known as direct electromethanogenesis. This metabolism is particularly noteworthy as in a methane producing MEC would allow storing electrical energy while producing a biofuel (Hara et al., 2013). So far, the main pathways occurring around the cathode in this methane synthesis within a MEC are unknown.

Hydrolytic and fermentative microbial communities also play a key-role in methane-producing MEC that are feed by complex organic mixtures, such as sewage sludge (Zeppilli et al., 2015). They hydrolyze and metabolize complex substrates (e.g. carbohydrates, proteins, lipids) and release reduced end-products such as C_1-C_{18} acids (e.g. acetate, propionate, lactate) and alcohols, H_2 and CO_2 in the medium. These compounds are available for other microorganisms such as anodic electrogenic microorganisms and planktonic microorganisms. Acetoclastic methanogens, which utilize acetate as electron donor instead of molecular hydrogen, is typically a type of metabolism that is less interesting in MECs as they compete with anodic electrogenic microorganisms. Nevertheless, thermodynamically, the anodic oxidation reaction should be favored compared with acetoclastic methanogenesis (Zhao et al., 2016).

The Figure 1 summarizes the main metabolic groups of microorganisms that can be found in a methane producing MEC.

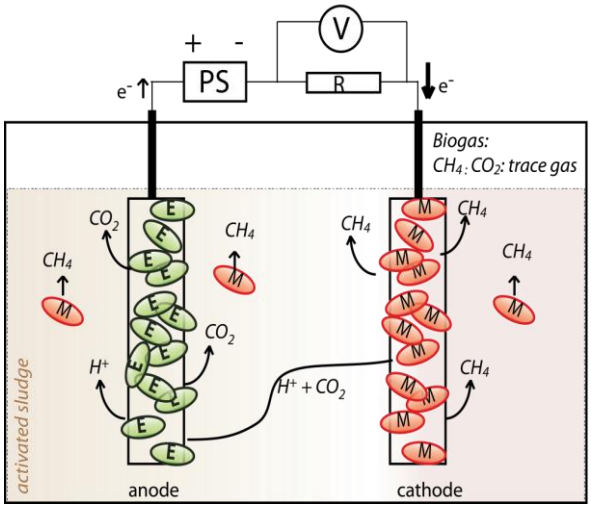

Figure 1: *MEC reactor with microbe. PS = power supply, V = voltmeter, R = resistance box, e- = electrons, VFA = volatile fatty acids (e.g. acetate, propionate, formate), E = electrogenic microorganisms on anode, M = methanogenic microorganisms on cathode and planktonic, F = fermentative microorganisms.*

Although the molecular mechanism of this reaction is still not clear, several studies have suggested that methanogenic archaea can directly take up CO_2, electrons, and protons to produce methane (Blasco-Gómez R. et. al, 2017). The concept “bioelectrochemical power-to-gas” (Geppert F. et al., 2016), encompasses bioelectrochemically produced methane through all catalytic processes taking place using renewable electricity.

In this project, we use two types of newly built microbial electrolysis cell reactors to find the best conditions to produce a biogas enriched in methane with the organic wastes remaining from the wastewater treatment plant of Châteauneuf in Switzerland. The scheduled plan was to start with a MEC stacked reactor (acronym MEC in the following text) to produce a good quality biogas and then a trickle bed reactor (TBR) to purify the biogas into pure methane (cf. Figure 2).

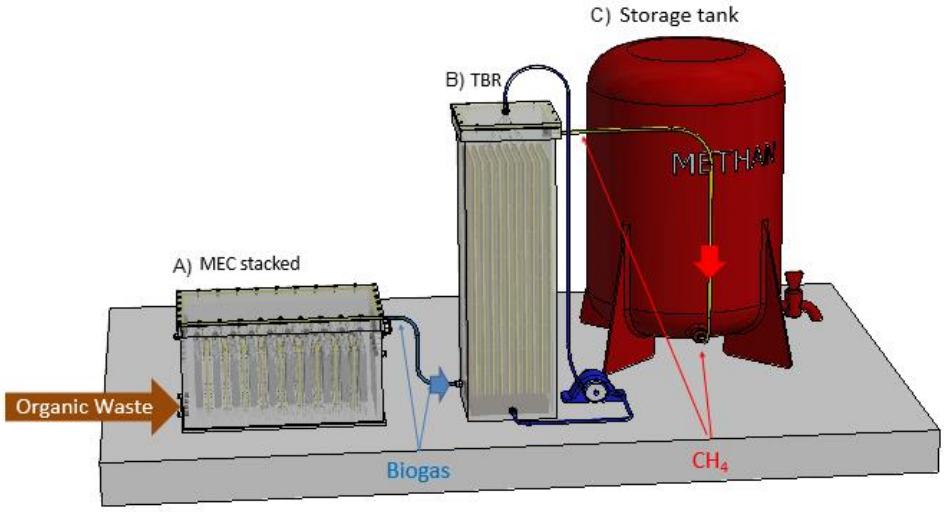

Figure 2: *Planned process set-up of the combined MEC reactors for methane production.*

Since the beginning of the XXIth century, the interest on bioelectrochemical systems (BES) has grown exponentially as shown on the following Figure 3.

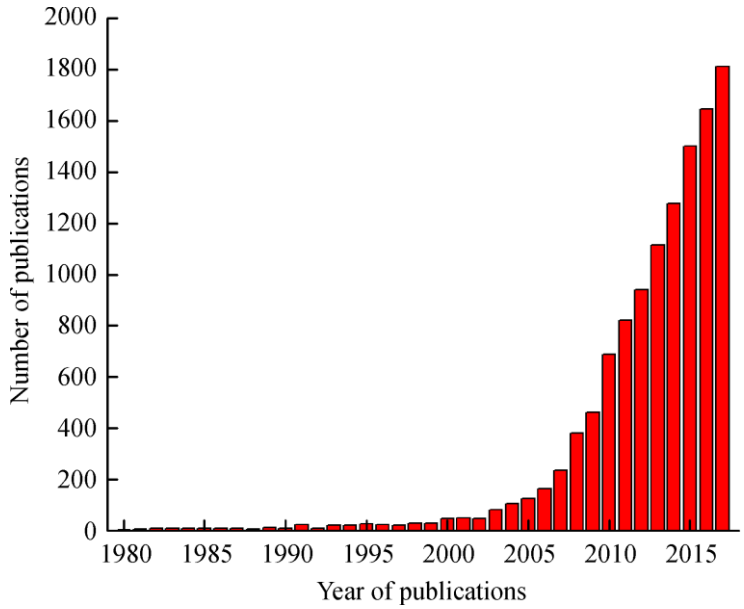

Figure 3: *Number of publications about BES technology since the 1980ties (Jain et al., 2018).*

Conversely, the bioelectrochemical methanogenesis only represents a small part of these research studies as presented on Figure 4.

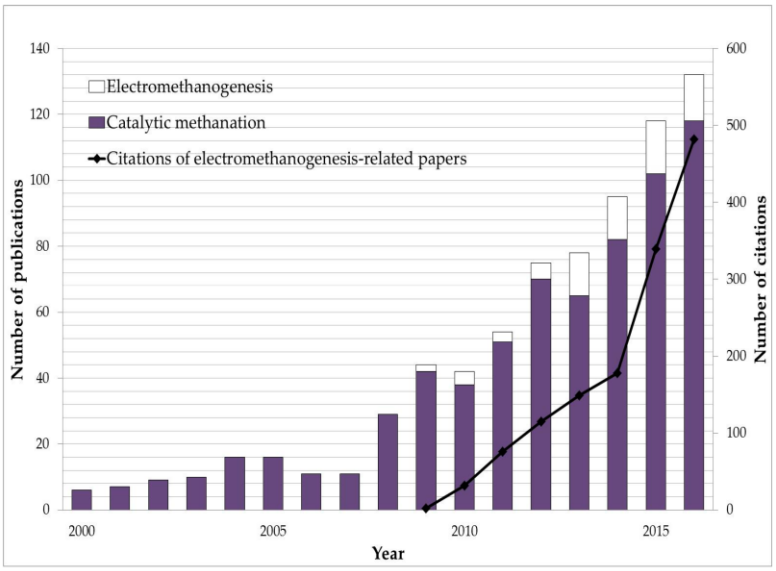

Figure 4: *Number of methane producing research publications in function of years (Blasco-Gomez et al., 2017)*

The following section resumes the results obtained by different researchers all around the world exploring MEC technology for biogas production also named bioelectrochemical methanogenesis.

Many publications see the promising results using MEC technology as form of anaerobic digestion. However, the results in literature are very heterogeneous because many of these studies were performed under favorable conditions. Most of them however, used synthetic substrates, targeted bacteria cultures, and divided electrochemical reactors in tow chambers (i.e. two-chambers reactors separated by an ionic exchange membrane or a diaphragm). In 2010, Villano achieved a methane production of about 7 ml in one day applying voltages between 0.6 and 0.9 V in a 0.5 liters two-chambers reactor filled with synthetic substrates. The methane fraction in the produced biogas was 76 ± 7 $\%_{mol}$. In this work, the cathodic potential was shown to be the driving force of the methanogenesis bioelectrochemical system (Villano et. al., 2010). A study published in 2015 by Zhen et al. achieved 2.30 ± 0.34 ml of methane production after 5 hours of potentiostatic applied voltage at 0.9 V (Zhen et al., 2015). Later, in 2018, Zhen et al. reached 15.16 ml of methane production in 24 hours by using carbon-based electrodes in a 200 ml reactor applying a constant voltage of 0.9 V (Zhen et al., 2018). Work conducted by Yin et al. in 2016 demonstrated that methane productions of about 700 ml in 72 hours of galvanostatic conditions was possible at a current density of 304.3 mA/m^3 in an anaerobic digestor and a microbial electrolysis cell coupled with a co-cultivation of the genus *Geobacter* and the genus *Methanosarcina,* respectively electrogenic and methanogen microbes (Yin et al., 2016). In 2018, Dou et al. achieved a methane production of 220.5 ml within 24 hours under potentiostatic conditions (i.e. E = 2.0 V) with a 2.1 liters two-chambered MEC-reactor filled with synthetic substrate. The methane fraction in the produced biogas was 88.5 %mol. The reactor used in this study was previously acclimatized with pure methanogenic cultures (Dou et al., 2018). In addition, there are numerous publications about parametric studies on bioelectrochemical methanization. For example, Sangeetha et al. found in 2017 that an electrochemical anaerobic digestor performs better in terms of methane production when the electrodes were placed at the bottom of the reactor because the organics removal was maximized with this electrodes' configuration (Sangeetha et al., 2017). Several works have also demonstrated that the addition of granulated activated carbon (GAC) in the substrates enhanced considerably the methane production by stimulating electron transfer reactions and electrotrophic methanogenic communities' development, principally thanks to its high specific surface (LaBarge et al., 2017). Other works have shown that a substrate's pH > 9.0 improves methane production by a factor of 1.5 compared to raw substrates pH. This phenomenon could be explained by the speciation carbon dioxide (CO_2) curve, since at alkaline hydrogen potentials, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) are favored to the detriment of CO_2 (Sun et al., 2015).

Electromethanogenesis-based technologies have a great potential for storing renewable energy in the form of methane, improving waste treatment processes, or upgrading gas streams containing CO_2. In all cases, future studies must focus on further up-scaling, increase process efficiencies, and reduce operation costs in order to compete with well-established technologies, or even a hypothetical outperformance. Those improvements will be achieved by targeting the current limitations of the electromethanization process such as side reactions, mass transport, inoculum type, electrode material, membranes, operation parameters, up-scaling, and the lack of novel efficient reactor designs. However, since these biofilms are dependent on several parameters such as the cathode potential, electrode material, pH, etc. only an extensive knowledge of how they interact between themselves will permit electromethanogenesis to be the basis of a competitive technology (Blasco-Gómez R. et. al, 2017).

Electromethanogenesis provides a new way to store electrical energy in a stable form as "carbon-neutral" methane becoming an attractive technology for bio-methane production and renewable energy storage (E-Jansen et. al, 2012). In this work, the bioelectrochemical process development was executed under real WWTP conditions by using pilot plant scale 50 liters reactors and raw waste sewage sludge from the Châteauneuf wastewater treatment plant (Sion, Switzerland).

2.2. Châteauneuf wastewater treatment plant

The municipal wastewater treatment plant (WWTP) of Châteauneuf is located in the Rhône Valley in Valais (Switzerland). The size in people equivalents is 66'667 (www.aquaetgas.ch). In this WWTP, the wastewater treatment consists of several separation steps (e.g. screening, sand removal) and the oxidation of the organic matter in aerated lagoons (cf. top of the Figure 5). During the wastewater treatment, several by-products are created (e.g. oily waste, primary sludge, activated sludge).
These organic wastes are treated further in the sludge treatment to reduce their volume and to recover energy by producing biogas in anaerobic digesters (cf. bottom of the Figure 5).

Primary sludge and activated sludge are mixed and disposed in a mixing tank before being thickened by a belt thickener. This thicken sludge is heated to 37 °C and injected in the Digester I, which has a volume of 2080 m^3. The daily injection of mixed thickened sludge is 100 m^3 per day and the mean retention time is about 20 days before being transferred to Digester II. This second digester is smaller (1090 m^3), is insulated but not heated and the mean retention time is about 10 days. Afterwards, the remaining sludge is transferred and stored in Digester III, before being dehydrated and grinded. The dehydrated and fully digested sludge is then incinerated.

In the Châteauneuf wastewater treatment plant, more than 450'000 m^3 of biogas is generated per year in Digesters I and II. The biogas is then co-generated into electricity and heated by coupled heat and power generation (CHP) and used to heat Digester I to 37 °C, the WWTP buildings and covers part of the electricity needed for WWT. The biogas contains 60-65 % of methane (CH_4) and the rest is mostly carbon dioxide (CO_2) with some trace gases (e.g. water vapor, H_2S) (pers. com. Vuillamoz, wastewater treatment technician).

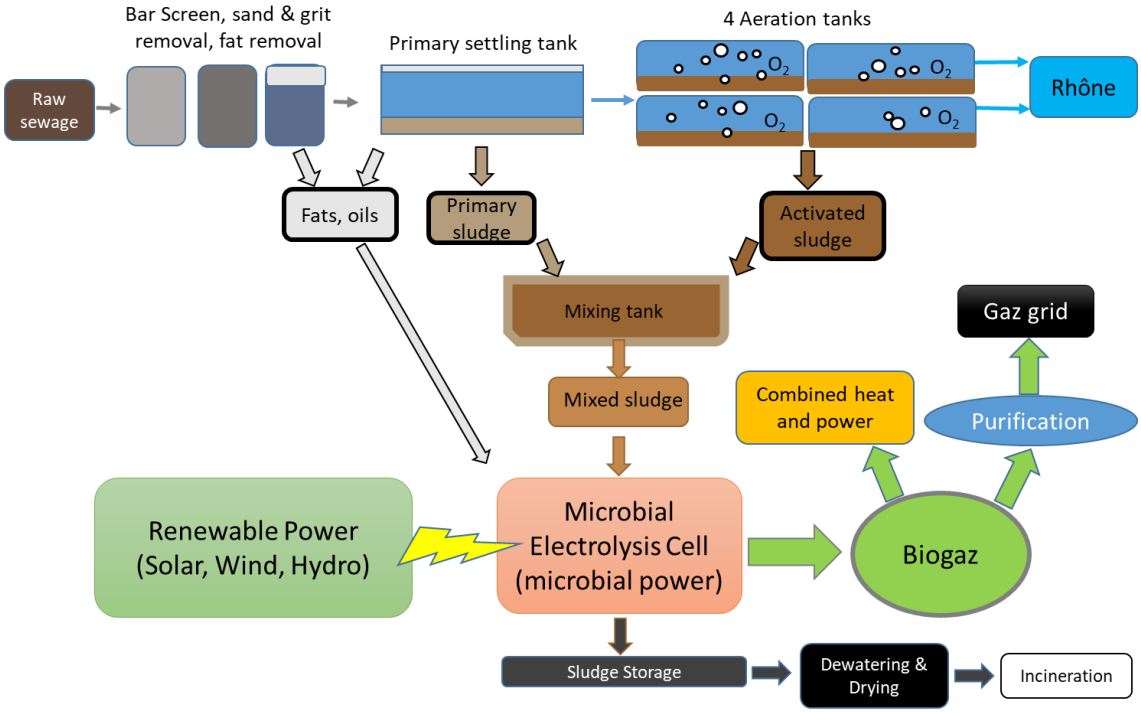

Figure 5: *The different steps of the wastewater treatment and sludge treatment as performed in Châteauneuf wastewater treatment plant. At the top is the water treatment and below are the sludge processing steps. Biogas is shown to be produced in future in a Microbial Electrolysis cell and then combusted to heat and electric power or injected to the gaz grid.*

3. General Conclusion & Perspectives

The different experiments demonstrated that MEC produced biogas with an increased content in methane compared to the standard digester in wastewater treatment plant (WWTP) of Châteauneuf, with the horizontal MEC reactor up to 78 % and 90 % with tower-MEC reactor using sewage sludge was achieved. These results are very promising, especially since the sludge introduced in our BES have not been pretreated neither heated-up. In WWTP, a large part of the biogas consumption produced by the digesters is used to heat-up the digester at 37 °C. This large difference in methane content between MEC and standard anaerobic digestion is not yet fully understood but it is believed that the MEC reactor system and particularly the electrode material could favor certain types of microorganisms and reactions.

In term of biogas production, the comparison between the WWTP and the MEC was not directly possible because the mixed sludge introduced in the Digester I undergoes a dewatering step after our sampling point. This additional step concentrates solid particles to 3-4 % TS while the mixed sludge introduced in the MEC is more diluted 0.3-0.5 %TS and this influences the methanogenesis rates. The biogas production rates are therefore more important per volume in the WWTP Digester. For a real comparison, dewatered mixed sludge should be introduced in MEC reactors, but this likely could lead to a clogging of the tubes due to the high solid contents.

As mentioned, the composition of the mixed sludge and digested sludge changes over the season and time in function of the waste quality and the operations done in the WWTP. Performing batch-experiment as we did so far, do not best represent fully the reality found in the WWTP. A proposition would be to move the MEC reactors directly to the WWTP of Châteauneuf and feed them continuously with fresh mixed sludge. This would likely improve the methanogenesis rates of both horizontal MEC and tower-MEC reactors. Some trials have been carried out on a continuous basis but this did not provide the same results as the continuous system at the WWTP with new sludge every daily and not as in this work with stored sludge.

Another factor that need to be controlled to understand the effect of the applied voltage on the MEC reactors is the temperature. During the complete set experiences using horizontal MEC & tower-MEC, it was observed that the temperature has an important influence on the biogas production. Higher temperatures promote the degradation of organic matter. The future reactors design should take into consideration that thermal isolation could improve the understanding of the involved processes and furthermore permit to optimize the operating parameters.

Several process parameters could be optimized to maximize the methane production, such as pH, the organic substrate content. However, one of the greatest advantages of this project is to operate under real conditions by using unpretreated sewage sludge from the municipal WWTP of Châteauneuf. In addition, cathodes and anodes are of high importance in the bioelectrochemical reactors and therefore it would be interesting to investigate different electrode material in order to identify the most appropriate one based on sustainable criteria.

Another important point to develop is to explore the “tower reactor” configuration of the Column-MEC in order to improve the methane fraction in the produced biogas. Therefore, several parameters need still to be assessed in the tower-MEC such as the reflux ratio (i.e. recirculation speed), the height of the bioelectrochemical reactor (i.e. ratio headspace: liquid) and the optimal sewage volume in the reactor.

To conclude, in this work, 10 liters of biogas with 80 %mol of methane was produced within 140 hours (i.e. 5.8 days) in a tower-MEC 50 liters bioelectrochemical reactor at room temperature, under anaerobic and semi-batch conditions and by applying a constant potential of 0.6 V (i.e. potentiostatic regime). Batch experiments under potentiostatic applications at different applied voltages have been conducted in order to identify an optimal potential for methane production from sewage sludge treatment in the column-MEC. The best biogas production rate was obtained by applying a continuous voltage of 2.0 V for 400 hours. The methane content in the biogas produced was of 75%. Therefore, further investigations are planned in order to be able to directly produce bio-methane (i.e. biogas with > 95 %mol methane content) with MEC & Column-MEC bioelectrochemical reactors developed in this project.

The MEC reactor was operated continuously. Under potentiostatic operation conditions at 1.2 V and 5 ml/min sewage sludge flowrate single pass circulation, almost 140 liters were produced in 1000 hours of process operation. The methane fraction reached was higher than in the batch experiments and reached maximum concentrations of 79%. The process has proven the ability of such reactors to be implemented in pilot scale directly at a wastewater treatment plant in order to have more homogeneity in the substrate. The sewage sludge flowrate was also investigated, and the results have shown that the higher the flowrate the higher is methane production. A methodology to identify and characterize the contributions of the biological methanization process and the electrosynthesis of methane was developed. In these experiences it was demonstrated that carbon dioxide is directly reduced into methane in MEC reactors. Moreover, very high current efficiencies were reached during voltage pulses (i.e. 83.3 %) and an enhancement factor was defined in order to assess a possible catalytic effect of the applied potential on the methane production process.

The metagenomic data of microbial community at the electrodes' surfaces was analyzed under different conditions. In general, it was demonstrated that the majority of the microorganisms are bacteria which are involved in organic matter degradation and syntrophic reactions leading to acetate and CO_2. The archaea identified were all related to the methanization since their metabolism uses hydrogen, carbon dioxide and acetate to produce methane. Precisely the biofilm developed on the cathodic surface was the most represented in terms of OTU indicating an important bioelectrochemical activity at this pole. Acetogens and in particular Acetobacterium was the most abundant bacterial genus in the biofilm at the cathode while Methanobacterium was the most abundant archaea genus. The influence of the applied voltage on the microbial population was not clear and metagenomics in the MEC and Column-MEC reactors should be further investigated.

The analysis of the inlet and outlet COD of the sewage sludge substrate has demonstrated the ability of the presented MEC systems to reduce the COD up to 97.4%. The results presented in this work suggest that the COD reduction in MEC reactors is exclusively driven by the biology while the methanization process which is also driven by the microorganisms activity needs to be catalyzed by an electrical energy input in order to reach a high COD conversion into methane that was up to 111% considering the entire bioelectrochemical system since when no potential was applied in the MEC reactors the COD conversion into methane was of 31%.

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