João Gonçalo Ferreira de Oliveira Dias

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Ammonium recovery from simulated and real agroindustrial liquid residues using bioelectrochemical systems

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Adviser: Professora Doutora Maria da Ascensão Carvalho Fernandes Miranda Reis , Full Professor,
NOVA University of Lisbon

Co-advisers: Doctor Alessandra Carucci, Full Professor, Università degli studi di Cagliari

Eng. Giovannimatteo Erby, Research fellow, IGAG-CNR

Doctor Stefano Milia, Researcher, IGAG-CNR

Examination Committee

Chairperson: Professor Doutor Mário Fernando José Eusébio
Raporteur: Doutora Nídia Dana Lourenço
Member: Professora Doutora Maria Ascensão Carvalho Fernandes Miranda Reis

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It's kind of fun to do the impossible.
Walt Disney

Believe you can and you're halfway there.
Theodore Roosevelt

Abstract

The increase concentration of nitrogen in wastewaters has led to economic and environmental consequences (such as high amount of energy and capital costs in wastewater treatment plants, eutrophication, high concentration of hazardous chemicals like nitrate, etc). Bioelectrochemical systems (BES) are able to remove and recover nitrogen in its ammonium form , from wastewaters while producing electricity or chemical products. BES use anaerobic bacteria to oxidize organic matter. The reaction releases electrons that migrate to the anode and, via an external circuit, reach the cathode where they react with oxygen, when using a Microbial Fuel Cell (MFC) or protons when using a Microbial Electrolysis Cell (MEC). These systems can be used to generate electricity (MFC), produce hydrogen or for nutrient recovery (MEC). In our process MECs were used to remove and recover nitrogen in its ammonium form , from wastewaters. The objective of this work was to determine the efficiency of MEC system in removing ammonium. Two MECs were used and both synthetic and real wastewaters were used as substrate. MEC1 and MEC2 worked at similar conditions except in the material used in the anode chamber: carbon felt in MEC1 and graphite granules in MEC2. When using the synthetic wastewater, MEC1 had a maximum removal efficiency and removal rate of 53,9% and 76,7 g $N-NH_4^+$ per square meter of the membrane per day, respectively, whereas MEC2 had 35,2% of removal efficiency and 29,7 g $N-NH_4^+$ per square meter of the membrane per day. When using real wastewater, MEC1 had a removal efficiency of 27,3% and removal rate of 56,4 g $N-NH_4^+$ $m^{-2}.d^{-1}$ whereas MEC2 had 24,6% and 19,1 g $N-NH_4^+$ $m^{-2}.d^{-1}$ for those same parameters. When comparing both systems, it's possible to see that, regardless the type of wastewater, the use of carbon felt (MEC1) allow to reach better performance.

Keywords: nitrogen, ammonium, BES, MEC, wastewater, removal, recovery

Resumo

O aumento da concentração de azoto em águas residuais tem levado a consequências ambientais e económicas (tais como, elevada necessidade energética e custos associados a estações de tratamento de águas residuais, eutrofização, elevada concentração de químicos nocivos, como nitrato, etc). Os sistemas bioelectroquímicos (SBE) conseguem remover e recuperar azoto na forma de ião amónia, produzindo ao mesmo tempo electricidade ou produtos químicos. Os SBE usam bactérias anaeróbicas para oxidar matéria orgânica. A reacção liberta electrões que migram para o ânodo e, através de um circuito externo, alcançam o cátodo onde reagem com oxigénio, quando se usa uma Célula de Combustível Microbial (CCM) ou reagem com protões, quando se usa uma Célula de Electrólise Microbial (CEM). Estes sistemas podem ser usados para gerar electricidade (CCM), produzir hidrogénio ou recuperar nutrientes (CEM). No nosso processo foram utilizadas CEMs para remover e recuperar azoto na forma de ião amónia, das águas residuais. O objectivo deste trabalho foi determinar a eficiência do sistema CEM em remover o ião amónia. Foram usadas duas CEMs e, como substrato, águas residuais sintéticas e reais. CEM1 e CEM2 trabalharam em condições idênticas, à excepção do material usado na câmara anódica: feltro de carbono na CEM1 e grânulos de grafite na CEM2. Quando se usou água residual sintética, a CEM1 teve uma eficiência de remoção e velocidade de remoção de $N-NH_4^+$ de 53,9 % e 76,7 g $N-NH_4^+$, por metro quadrado de membrana, por dia, respetivamente. Para a mesma água residual, a CEM2 teve 35,2% e 29,7 g $N-NH_4^+/(m^{2*}\text{dia})$, para os mesmos parâmetros. Quando se usou água residual real, a CEM1 teve uma eficiência de remoção de 27,3% e uma velocidade de remoção de 56,4 g $N-NH_4^+/(m^{2*}\text{dia})$ enquanto, para os mesmos parâmetros a CEM2 teve 24,6% e 19,1 g $N-NH_4^+/(m^{2*}\text{dia})$. Ao comparar os dois sistemas conclui-se que, independentemente do tipo de água residual, o sistema que usa feltro de carbono (CEM1) tem uma melhor prestação.

Palavras-chave: azoto, ião amónia, SBE, CEM, água residual, remoção, recuperação

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State of the art

1.1 Nitrogen: from discovery to the synthesis of ammonia

Nitrogen was officially discovered in 1772, by the scottish scientist Daniel Rutherford. Other scientists also discovered it independently, such as Carl Scheele, Henry Cavendish and Joseph Priestley [1]. Also, in the 18th century, nitrogen species were found and in the 19th, it was discovered how the species transformed into one another. In 1823, Johann Wolfgang Dobereiner synthesized ammonia for the 1st time, using nitrogen and hydrogen and a platinum catalyst. However, it was inefficient and couldn't be produced in larger scale [1].

The existence of a nitrogen cycle was first described in 1856, by Jules Reiset, with the observation of the release of nitrogen from decaying organic matter. After this discovery, the microbes role in the transformation of nitrogen into different species was established and with it, the processes of nitrification, biological nitrogen fixation and denitrification. The biological nitrogen cycle and all the conversion into the different species of nitrogen were identified, by the end of the 19th century [1]. In the 20th century, the anammox (anaerobic ammonium oxidation) process and the organisms that take part in it were discovered. In the annamox process, ammonia (NH_4^+) and nitrous dioxide (NO_2) react to form nitrogen (N_2) and water (H_2O) [2]. This process can occur even at lower temperatures than 15ºC or higher than 40ºC [3].

Equation of the Anammox process:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad 1.1$$

The well-known Haber-Bosch process was found in the early years of the 20th century. It combined the laboratory work of the german scientist, Fritz Haber, and the engineering mind of Carl Bosch. Fritz Haber first discovered the optimal conditions for laboratory scale production of ammonia; years later, Carl Bosch found how to get nitrogen and hydrogen at low cost, and designed equipment strong enough to withstand the high temperatures of the process. The ideal operation conditions for this process are 200-400 atm and 400-650ºC [2]. By 1913, the first plant was founded and was producing 10 tons of ammonia per day [1].

Base equation of the Haber-Bosch process:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad 1.2$$

The nitrogen cycle, as we know it in our days, is represented in figure 1.1.

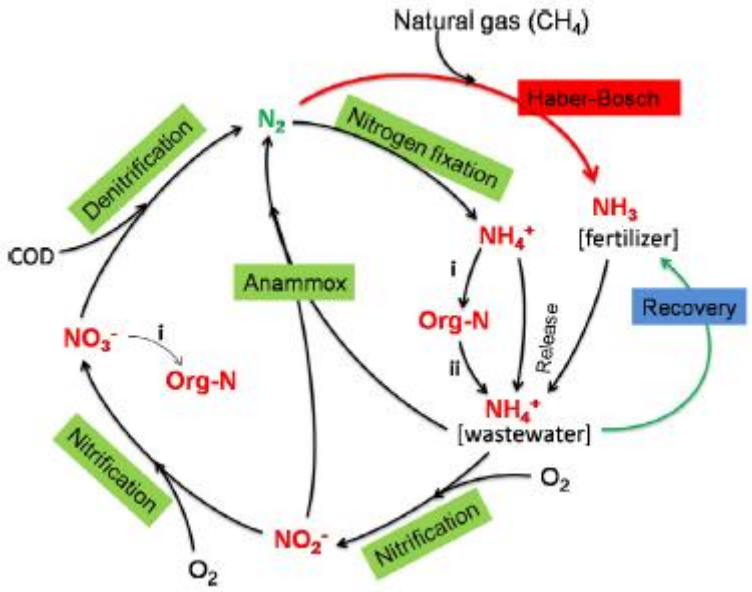

Figure 1. 1 - Simplified nitrogen cycle with major natural and anthropogenic processes. i)assimilation; ii) ammonification [2].

1.2 Nitrogen: pollution issues and health hazards

A study done by the Princeton University conclude that the fast increase in world population would rise the actual number (7.6 billion, in 2018) in the order of 2 or 3 billion people, by 2050 [4]. This growth leads to an exponential need of bigger amounts of food and ultimately also of fertilizers [4]. The global consumption of fertilizers was estimated with a growth of 1.8% year, in 2018. The main nutrients in fertilizers include nitrogen, phosphorous and potassium. These nutrients have been having annual growths of 1.5% (nitrogen), 2% (phosphorous) and 2.9% (potassium), per year [5]. Furthermore, when used in excess, nitrogen is left in the sub levels of the ground and in the air. There, in the air, it can form nitrous oxide, a greenhouse gas and ozone-depleting gas and, in lakes and rivers, can over enrich and contaminate them [4,6] .

The accumulation of ammonia in the lakes or rivers leads to a exponential growth of algae and bacteria, this phenomena is called eutrophication [7]. Eutrophication starts with the growth of a layer of algae bloom that fills the surface of the water body. The sun is unable to reach the plants in the lower levels of water and unable of doing the photosynthesis, these plants die. As they die the bacteria present in the water feed on them and consume the oxygen present in the water, and release even more nutrients into the water[8]. The bacteria keep feeding and growing to bigger and more complex bacteria. At some point, the water runs out of oxygen and becomes anoxic and so, impossible to sustain plant and animal life [9] .

Nitrate (NO_3) is a product of the biological reaction of nitrification between ammonia and bacteria in the presence of oxygen and it is naturally produced in water bodies and can be found in food and water. However, water bodies that have been poisoned with excess amount of nitrogen will have their levels of nitrate rose above the health limit which is 11.3 mg per liter. If the nitrate concentration rises above 50 mg/L then some health risks might appear such as conversion of hemoglobin to methemoglobin. When this condition happens, the pacient has his oxygen levels decreased [10]. It has also been reported that the consume of nitrogen enriched water can lead to thyroid enlargement, varied types of cancer and even two kinds of birth defects [10].

1.3 Nitrogen: Removal and Recovery

As previously presented, it is essential to the environment the possibility to remove the ammonia from the water. There are biological processes including conventional and advanced approaches, and also physical and chemical processes.

1.3.1 Biological processes

The biological processes include nitrification and denitrification (conventional processes) and more advanced processes such as anammox, SHARON, CANON and CANDO.

1.3.1.1 Conventional

The two main biological removal processes are nitrification and denitrification.

Nitrification is the conversion process of ammonium to nitrate. It happens in two steps with two different autotrophic bacteria species [11] . *Nitrosomonas*, that converts ammonia and ammonium to nitrite and *Nitrobacter* that converts nitrite to nitrate. The steps are sequential but happen at a very fast rate, so nitrite levels at any point are usually very low [12]. These bacteria species are aerobic so the water environment needs to have oxygen dissolved [11,12]. The nitrification reaction lowers the pH of the surrounding environment because it releases protons. It is important to know that nitrification has specific operating conditions regarding pH and temperatures. The optimal conditions for bacterial activity are between 7.5 and 8.5 and 30-35ºC for pH and temperature, respectively [12].

The nitrification reactions occur as follows, in two steps, with *Nitrosomonas* and *Nitrobacter* being involved in the first and second steps, respectively:

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^- \quad (1.3)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (1.4)$$

Nitrification is a zero-order reaction, regarding ammonium concentration as long as it is between 1 and 5 mg/L [12]. Using the Monod equation to describe the kinetics of the oxidation of ammonium to nitrite we have:

$$u_N = \frac{u * N}{K_N + N} \quad (1.5)$$

Where:

u_N – growth rate of *Nitrosomonas*

u – maximum growth rate

N – ammonium concentration, mg/L

K_N – N concentration at which u_N = 0.5u, mg/L

The conversion of nitrite to nitrate is also consider a zero-order and *Nitrobacter*'s maximum growth rate is greater than that of the *Nitrosomonas* [11].

Some of the limits that keeps nitrification from happening is the great change in pH and temperature; pH lower than 6 will stop nitrification as well as with temperatures above 40ºC. At temperatures below 20ºC the nitrification rate will slow considerably and at lower than 10ºC it will cease and only resumes after a great increase in temperature [12].

The conversion of nitrate to nitrogen (N_2) is called denitrification. For denitrification to occur, anoxic conditions and a source of carbon must exist. The process is assisted by heterotrophic bacteria, like *Bacilus denitrificans*, *Micrococcus denitrificans*, *Pseudomonas stutzeri*, and *Achromobacter* [11], that feed of the oxygen present in the nitrate molecules, then convert it to nitrous oxide (N_2O) and ultimately to N_2. Unlike nitrification, the denitrification provides alkalinity and not acidity. Its optimal conditions are with pH range of 7.0-8.0 and temperatures between 5 and 30ºC [11]. The process also benefits from the presence of methanol or acetic acid [11].

The denitrification reaction occurs as follows [12] :

$$6NO_3^- + COD \rightarrow N_2 + CO_2 + H_2O + 2OH^- \quad (1.6)$$

Where COD is the source of carbon and stands for Chemical Oxygen Demand. Here is the amount of oxidazable matter from which the bacteria can feed on and is measured as the amount of oxygen equivalents (mgO_2/L).

The denitrification rate can be determined as shown in equation 1.7:

$$U_D = \frac{-d(N-NO_3)}{Xdt} = k_D \frac{(N-NO_3)}{K_D + (N-NO_3)} * \frac{C}{k_C + C} \quad (1.7)$$

U_D – Denitrification rate (mg N-NO_3/mgSSV.d);

(N-NO_3) – nitric nitrogen concentration (mg N-NO_3);

X – microorganisms' concentration (mg SSV/L);

k_D – maximum rate of nitrate consumption (mg N-NO_3/mg SSV.d)

K_D – nitrate's saturation constant (mg N-NO_3/L). (K_D= 0.1 mg N-NO_3/L);

C – Carbon concentration (mC/l);

K_c – Organic carbon semi-saturation constant (mC/l).

1.3.1.2 Advanced

More advanced biological techniques for nitrogen removal, than conventionals include:

- Anammox
- CANON
- SHARON
- CANDO

The Anammox process was discovered in the 90s and works in anaerobic conditions [13]. In this process, Anammox bacteria oxidize ammonium to nitrogen gas, with nitrite as the electron acceptor. The inorganic carbon (CO_2) present in this process is used by anammox microorganisms for their growth. The improvement of this process when compared with conventional nitrification/denitrification is remarkable since it consumes 100% less biodegradable organic carbon and at least 50% less oxygen (which lowers the capital costs). The equation of this process is given by [14]:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (1.8)$$

If the anammox is combined with a pre-nitrification step, only a part of the ammonium will need to be nitrified to nitrite, while Anammox process combines remaining ammonium with the nitrite

to dinitrogen gas. It is this step that reduces the oxygen demand and solves the problem of nitrite supply for anaerobic AOB (Ammonia Oxidizing Bacteria) and high concentration of nitrate in treated waters [15]. The Anammox can sustain at high nitrogen loads and has already been employed in full scale treatment plants. Nowadays, Anammox is being used, for example, for treating sludge digestion supernatant [15].

The CANON (Complete Autotrophic Nitrogen Removal Over Nitrite) process can remove ammonium from wastewater in a single, oxygen-limited treatment step. It relies on two big bacteria populations, *Nitrosomonas* and *Planctomycete* ammonium oxidizing bacteria, the first working in aerobic conditions and the second in anaerobic. In Third *et al*, 2001 experiment it was possible to remove 92% of nitrogen from a water body at a removal rate of 0.1 $kgN.m^{-3}.d^{-1}$. If nitrification takes place, the *planctomycete*-like anammox bacteria can use nitrite as electron acceptor and produce dinitrogen [16], as shown below:

$$NH_4^+ + 1.3NO_2^- \rightarrow 1.02N_2 + 0.26NO_3^- + 2H_2O \quad (1.9)$$

In this study, removal rates went up to 1.5 $kgN.m^{-3}.d^{-1}$, showing that the CANON could be a very useful nitrogen removal process for high strength ammonium wastewaters. Furthermore, the ability of the CANON system to withstand ammonium limitation for a long period (in this case, one month), proved that it was a robust and effective industrial system to remove ammonium from wastewaters with a very low organic load. Anammox CANON has similar results to the SHARON process but has a great advantage that is consuming 63% less oxygen and 100% less reducing agent than conventional removal systems [13]. Some other advantages include savings in carbon sources and aeration costs, but it still has an issue to be handled, that is the enrichment of anaerobic microorganisms capable of oxidizing ammonia with nitrite as electron acceptor.

The SHARON process is used to remove ammonia from wastewaters and works at a temperature of 30-40ºC and a pH range of 7-8. The absence of sludge retention prevents nitrite oxidation, lowering the capital costs. The pH in this system is controlled by denitrification. The high temperature has two advantages: first, it enables specific growth rates leading to no sludge retention; secondly, unlike most of the wastewater treatment plants that work at 5-20 ºC, temperature that benefits growth of nitrite oxidizers instead of ammonium oxidizers, the higher temperature favors the growth of ammonium oxidizers [17].

CANDO, or Coupled Aerobic-anoxic Nitrous Decomposition Operation, is used to convert ion form ammonium into gaseous nitrogen while simultaneously generating power and potentially recovering nutrients. It involves in 3 main steps: 1) biotic conversion of ammonia to nitrite, 2) abiotic/biotic conversion of nitrite to nitrous oxide and finally 3) decomposition or combustion of nitrous oxide to nitrogen, oxygen and energy [18]. When using Fe (II) the conversion efficiency of NO_2^- to N_2O can be over 90%, with 98% nitrogen removal from water. Regarding this system it is noteworthy to indicate that the first and third steps have already been done in full-scale. The second is more complicated to be applied in full scale processes. However, Scherson *et al*, 2012, did succeed in using Fe (II) to abiotically reduce NO_2^- to N_2O or to do it biotically with PHB (polyhydroxybutyrate) storage granules. This system has the potential to lower aeration and biosolid production, the two major operational costs [18].

1.3.2 Physical and chemical processes

The following 4 processes are the most common when it comes to ammonia recovery and concentration:

- Ammonia stripping
- Ionic exchange
- Membrane filtration

- Struvite precipitation

1.3.2.1 Ammonia stripping

This process is conduct as a liquid-gas stripping, which means that the ammonia is going to have its mass transfer from liquid phase to gas phase. It is usually done with high ammonia concentration solutions and requires pH above 9.5 and temperatures over 80ºC. It requires also an extractant gas that usually is air; the high temperature and pH of this process allows the operation to run properly without a need for an elevated amount of air. After stripping, ammonia can be captured, for example, through absorption to produce a high concentrated fertilizer product. When a stripping column is connected with an absorption column, the second usually contains a strong acid, like sulfuric acid, and the absorption takes place by mixing the ammonia and sulfuric acid which leads to ammonia sulphate. This absorption process has usually a yield of 80-90%, sometimes even more [19].

1.3.2.2 Ionic Exchange

Like the name suggests, ionic exchange consists in the movement of ions, in this particular case from the solvent, to the charged surfaces of the insoluble, rigid sorbents suspended in a vessel or packed in a column [19]. This process can be used to recover nutrients such as P, N and K, but it is mostly used in wastewaters where their concentrations don't exceed 2000 mg/L and solid concentrations are lower than that value [19].

In this process, a microporous exchange resin is of outmost importance for it is in this resin that the ions are going to be bound while the water passes through the membrane. This resin can be made of a variety of material being sulfonated polystyrene the main choice for water softening, for example. From time to time, this membrane has to be replaced or regenerated since it becomes saturated over time [20]. Sodium hydroxide and hydrochloride acid are the most common chemical regenerants.

Ionic exchange is a good option when treating wastewaters enriched with ammonia because it can be done with a great variety of temperatures and responds well when sudden loadings of ammonia take place, unlike biological processes [20]. There are two types of resins: natural (zeolites) and synthetic resins. Zeolites are natural products, don't represent a threat to the environment, have high ion exchange capacity, selectivity and a very low cost comparing to synthetic resins. Synthetic resins based on organic compounds are very selective but this makes them very expensive, for example, silica powder [20].

1.3.2.3 Membrane filtration

Membrane filtration is a separation process that consists in the selective separation of compounds from one solution to the other, with the aid of a membrane. This process can be sub-divided in five: microfiltration, nanofiltration, ultrafiltration, electrodyalisis and reverse osmosis, dependind on the type of separation. The first three only depend on the size of the component that one wants to separate, the other two will be explained in detail. These processes require a pre-treatment of the solution so that issues like fouling don't occur and also to ensure maximum life time of the membrane and higher flux rates [19].
Reverse osmosis and electrodyalisis have been used in the recovery and concentration of ammonia from swine wastewater, by Mondor et al, 2007. In this work, a maximum concentration of 13 g/L was achieved for both processes being membrane fouling and volatized ammonia their biggest issues [21].

In an electrodyalisis, charged ions move from one solution to the other crossing a specific and selective membrane. In a CEM, Cation Exchange Membrane, only positively charged ions can pass from one solution to the other, whereas in an AEM, Anion Exchange Membrane, only anions, negatively charged ions can pass. This process allows the concentration of differently charged species [19].
Reverse osmosis, on the other hand, works when providing energy to a system and a pressure above the osmotic pressure, so that the high concentrated solution migrates to the part where there is a solution with lower concentration, through a semi-permeable membrane, the reverse of the normal osmosis. Reverse osmosis is mostly used to desalinate, demineralize or deionize a solution [22]. In reverse osmosis, a pressure is applied on the solution with the salts that are pushed against the membrane, leaving 90-95% of the salts behind the membrane and in front of the membrane will be water. The pressure applied is as great as the concentration of salt in the water [22].

1.3.2.4 Struvite Precipitation

Struvite is the common name for magnesium ammonium phosphate and is naturally produced in wastewater treatment plants, in joints and pipes. It is necessary that the ions Mg^{2+}, NH_4^+ and PO_4^{3-} are with equal moles. These 3 reagents react with water to form struvite, as it is described in the following equation:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + 2H^+ \quad (1.10)$$

Typically, struvite contains 12% of P and 5% of N with almost no heavy metal or biological contaminants. Although struvite precipitation is a process that works better when removing P (80-90%) it can also remove ammonia, from wastewater (20-30%). It does not work as good as with phosphorous because there is a large molar amount of ammonia in the common wastewaters that keeps the system from achieving the needed molar stoichiometry equality [19] .Struvite is a viable process since it is known to be a slow release fertilizer and its production helps preventing unwanted precipitates in wastewater treatment plants. This process depends highly on the pH, temperature, molar ratio of magnesium, phosphate and ammonium, among others [23].

1.4 Bioelectrochemical systems (BES)

A bioelectrochemical system works through the oxidation of organic compounds in the wastewater by electrogens, like bacteria, growing in the anode, producing a current through an external circuit [24].

A bioelectrochemical system, (BES) is a technology that uses microorganisms to catalyze redox reactions at the electrodes. In the last 10 years, BES attracted the scientific community interest for the possible applicability on wastewater treatment [25], and on metal [2] and nutrients removal [26].

In general, in BES systems anaerobic bacteria oxidize the organic matter in the wastewater to CO_2, by using the anode as electron acceptor (Modestra *et al.* 2015). The anode oxidation reaction can be represented by the acetate or glucose degradation, 1.11 and 1.12 equations [2]:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad (1.11)$$

$$C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 30H^+ + 24e^- \quad (1.12)$$

The organic matter degradation operated by microorganisms release electrons that are transferred to the anode. The electrons produced from this oxidation can be transferred to the anode in three ways, so far: direct contact, nanowires produced by bacteria and mobile electron shuttles. The electrons move from the anode to the cathode by an external circuit. This electron flow is then compensated by an ion flow from the anolyte to the catholyte, where they find the electron acceptor (i.e. oxygen, NO3, ferricyanide for MFCs or hydrogen ions for MECs).

Due to different kinds of reaction that happen at the cathode, BES can be divided in Microbial Fuel Cell and Microbial Electrolysis Cell. MFC is used to generate electricity [27] whereas an MEC is used for hydrogen production and/or recover of nutrients [28]. One of the differences between the two BES, regarding ammonia recovery, that falls in favor of the MEC, was described in Liu, 2016 [24] and informs that ammonia recovery is greatly enhanced when the current density is also high. This led to better performances recovering ammonia from wastewaters using MEC than MFCs, if an external power source was used.

The two different cathode reactions that are the main difference of these two cells are described as follows by equations 1.13 (MFC) and 1.14 (MEC) [27,28]:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (1.13)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1.14)$$

The oxidation releases protons and these particles increase the acidity of the anode chamber. On the other hand, the product of cathode reactions releases hydroxile groups (OH^-) that increase the alkalinity, instead of the acidity. To reach a pH equilibrium, between the anode and cathode chambers, a migration of cations from the anolyte to the catholyte takes place.

Regarding the configuration, a BES can be structured in single or double chamber.

In the double chamber configuration, anode and cathode chambers are physically separated through a membrane, that can be a Cation Exchange Membrane (CEM) or an Anion Exchange Membrane (AEM).

The CEM and AEM membranes are semi-permeable membranes with one main selective goal: the migration of a specific type of ions. A CEM, as the name suggests, allows the passage of cations, but blocks anions. On the other hand, an AEM membrane allows only the passage of anions, blocking the cations.

In the single chamber configuration there is no separation between anode and cathode chamber, and both the electrodes share the medium.

In figure 1.2 there are the two principal types of Bioelectrochemical systems, MFC and MEC:

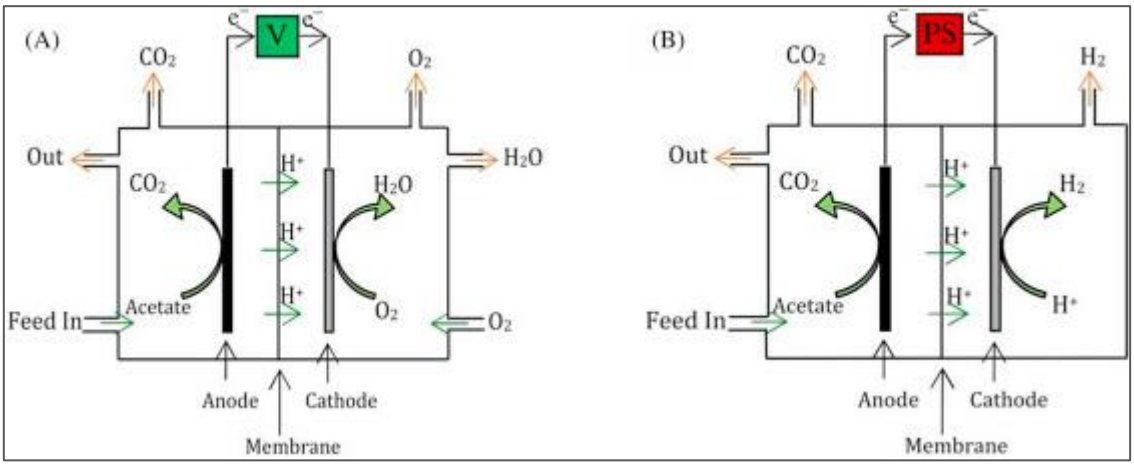

Figure 1. 2 - Scheme of an MFC (A) and an MEC (B) [28]

1.5 Microbial Fuel Cells (MFC)

AN MFC is capable of oxidizing both organic and inorganic matter, through bacteria activity and use the chemical energy stored within the substrate to generate electric current. This phenomenon was first observed by Potter, in 1911 [29]. Unlike a normal biofuel cell, an MFC does not require a mediator, like an electron shuffle, to generate electricity. Although the use of another kind of mediators, called electron relays (or redox mediators) facilitate, not the electricity generation but the transport of electrons, because most of the bacteria used in an MFC are electrochemically inactive [30]. In an MFC, the current generation is not spontaneous without an electron acceptor like oxygen, ferricyanide, nitrates, etc, which needs to be present in the cathode.

A schematic representation of a two-chamber MFC, using glucose as substrate is shown below:

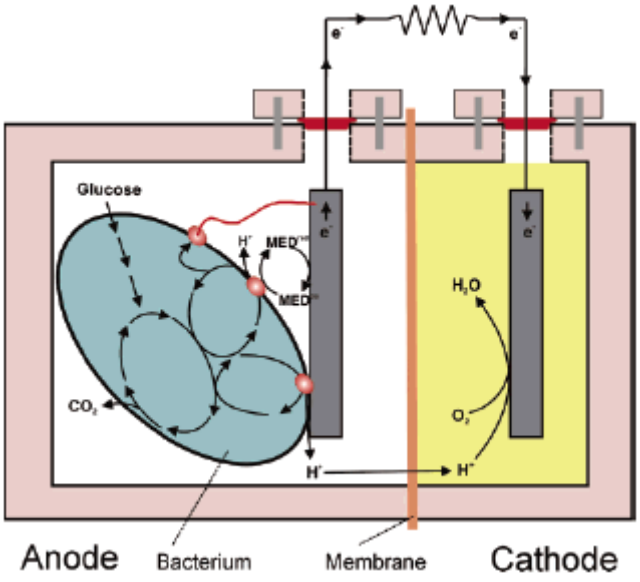

Figure 1. 3 - Scheme of an MFC [28]

1.5.1 Configurations

The MFC technology is expanding and, in the process, different materials are being used and in a great variety of configurations. Some of these configurations and materials will be approached here. These configurations also work under different conditions and parameters like pH, electron acceptor, operation time and temperature [27].

The most common MFC equipment is the "H-shape" because it is cheap and well suited for most of the common basic experiments that are testing the power production, with new materials or microorganisms cultures, suited for the oxidation of a specific substrate. This shape has two bottles connected by a tube that contains a CEM (e.g. Nafion) [27].
However, H-shape MFC isn't the only option. Another alternative, and an inexpensive one, would be to connect, and bend through heat, two tubes and thus there would be an U-shape MFC. This one is usually filled with agar and salt, working both as an exchange membrane. This shape represents a poor choice because the presence of salt is responsible for high internal resistance resulting in a low power production [27].

Other examples of MFC that have already been used are shown in the following figure, taken from the work of Logan, 2006: in A, we have a system with a salt bridge (shown by arrow); in B, a four batch-type MFCs with chambers separated by the membrane and held together by bolts; in C, the set-up is the same as in B but with a continuous flow-through anode (granular graphite matrix) and close anode-cathode placement ; in D, a photoheterotrophic type MFC, single-chamber, air-cathode system in a simple "tube" arrangement; in E, a single chamber, air cathode system in a simple "tube" arrangement and in F, there is a two chamber H-type system with anode and cathode chambers equipped for gas sparging [27].

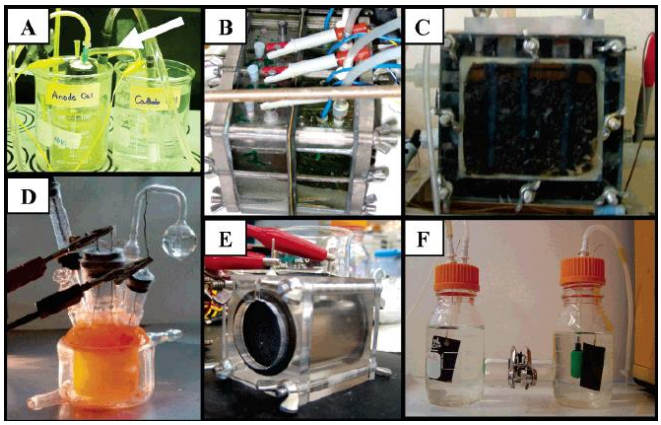

Figure 1. 4 - Different examples of known MFCs [26]

1.5.2 Components

Cathode

The choice of cathode materials influences the system performances. Generally, it has been observed low efficiency with oxygen paired with carbon electrodes. Platinum catalyzers have been widely used to increase kinetic reactions [27].

Electron acceptors

One of the most common materials for a cathode is the ferricyanide ($K_3(Fe(CN)_6)$). The biggest advantage of this widely used electron acceptor is the fact that, if combined with a plain carbon

electrode then the overpotential (loss of energy) is very low. The disadvantage is the need for replacement of the catholyte due to insufficient reoxidation by the oxygen [27].

Although ferricyanide is a good candidate as electron acceptor, the best electron acceptor to use is oxygen. The fact that it has no cost associated and the only product from its reaction is water are some of the reasons why this is the best suited substance. Also, oxygen exists in great abundance and with the use of water there is no risk of production of hazardous species [27].

Anode

When choosing the material of an anode it is important to guarantee that it is conductive and biocompatible (since there will be microorganisms present in this chamber) and chemical stable in the reactor solution. Logan, 2006 describe, in the use of metal anodes, non-corrosive like stainless steel. For the electrode, carbon is the most used. It can be in the forms of plates, rods, glassy paper, felt or brushes [27]. Carbon shaped in plate or rod is the most common because of their low cost, defined surface area and easier to handle than the others.

Membrane

The membrane must allow the transition of protons from the anolyte to the catholyte but keep the oxygen or any other electron acceptor in the cathode, not allowing their passage (this occurs in the presence of a CEM; if an AEM is used, the process is different and the hidroxile groups (OH^-) will migrate to the anode, from the cathode).

It is important to remember that an MFC produces water in the cathode but in the anode, there are anaerobic bacteria. Because of this, we conclude the importance of the existence of a membrane in the prevention of migration of water or oxygen from the cathode chamber to the anode chamber. This migration would lead to total malfunction of the MFC and death of the microbial organisms.

The most used membrane is Nafion because of its small cost compared to the others in the market, like Ultrex or plain salt bridge. Salt and agar were discovered to be a bad option after some experiments because they cause high internal resistance that leads to low power densities.

Ion exchange membranes is a field of expertise that is continuously growing and some of the main goals include long-term stability and performance [27].

1.5.3 Principles of voltage generation in MFCs

In order to have electricity production, the overall reaction of the MFC has to be thermodynamically favorable [27].

This reaction can be explained through the Gibbs free energy variation (J), shown in equation 1.15 [27]:

$$\Delta G_r = \Delta G_r^{\circ} + RTln(\prod) \quad (1.15)$$

Where,

ΔG_r – Variation of Gibbs free energy (J)

ΔG_r° - Gibbs free energy under standard conditions (298.15K, 1 bar) (J)

R – Perfect Gases constant (8.314 J mol^{-1} K^{-1})

T – temperature (K)

∏ - without units, is the reaction quotient calculated as the activities of the products divided by those of the reactants

However, in an MFC analysis the calculations are made considering the energy involved in the electromotive force (emf), E_{emf}(V), as work produced by the cell (W) [27]:

$$W = E_{emf}Q = -\Delta G_r \quad (1.16)$$

Where,

W – work produced by the cell (J);

Q – charge transferred in the reaction (C);

This equation gives us the potential difference between the cathode and the anode.

This charge transferred in the reaction is given by the number of electrons exchanged in the reaction and can be calculated as shown [27]:

$$Q = nF \quad (1.17)$$

Where,

n – number of electrons per reaction mol;

F – Faraday constant ($9.64853*10^4$ C/mol)

If we combine the equations 1.16 and 1.17 we obtain [27]:

$$E_{emf} = \frac{-\Delta G_r}{nF} \quad (1.18)$$

If we consider standard conditions, ∏=1 so we have [27]:

$$E^{\circ}_{emf} = \frac{-\Delta G^{\circ}_r}{nF} \quad (1.19)$$

From this equation we can obtain a way to calculate the electromotive force of the cell [27]:

$$E_{emf} = E^{\circ}_{emf} - \frac{RT}{nF} ln(\prod) \quad (1.20)$$

Where,

E°_{emf} - standard cell electromotive force (V)

The great advantage about using this equation is that if the value is positive then the reaction is favorable, and it also gives the *emf* for the reaction. One thing to consider is that this value, *emf*, is a theoretical value. Since the system present various losses this value only represents the maximum possible of the *emf* [26].

In the following equations we can see a way of calculating the emf of each part of the cell, anode and cathode, in presence of acetate as electron donor [27].

$$E_{An} = E_{An}^{\circ} - \frac{RT}{8F}\ln\left(\frac{(CH3COO^{-})}{(HCO3^{-})^{2}(H^{+})^{9}}\right) \quad (1.21)$$

Where:

E_{An}° - standard anode electromotive force (V)

Considering the acetate reaction [27]:

$$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O \quad (1.22)$$

Also, the electromotive force in the cathode can be obtained, with equation 1.23 [27]:

$$E_{Cat} = E_{Cat}^{\circ} - \frac{RT}{4F}\ln\left(\frac{1}{pO_2(H^{+})^{4}}\right) \quad (1.23)$$

Where,

E_{cat} – cathode electromotive force (V)

E^{o}_{cat} – standard cathode electromotive (V)

p_{O2} – partial pressure of oxygen (bar)

(H^{+}) – concentration of hydrogen (M)

R – perfect gas constant (8.314 J mol^{-1} K^{-1})

T – temperature (K)

F – Faraday's constant ($9.64853*10^{4}$ C/mol)

Equation 1.23 follows the classic reaction that occurs in the cathode, if we use oxygen as an electron acceptor, that is described as follows, by equation 1.24 [27]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (1.24)$$

By subtracting to the cathode emf the anode emf, we get the total theoretical emf of the cell (equation 1.25) [27]:

$$E_{emf} = E_{cat} - E_{An} \quad (1.25)$$

This was just one example. There are other cathodes that can be used and the system can work in different conditions. So, since the equations above depend on all these factors it is to be expected different emf and power output when parameters are changed.

1.5.3.1 - Potential losses

All the equations described above represented only a theoretical *emf*. This is because the system is subject to flaws and as these happen some potential losses might occur. To understand these losses, first we must know what is an Open Circuit Voltage (OCV). The OCV can be described as

"the cell voltage that can be measured after some time in the absence of a current" [27]. Because of these potential losses, OCV is always lower than the emf calculated.

The factors that reduce the cell voltage (overpotentials) are [27]:

1. Anode losses
2. Cathode losses
3. Ohmic losses
    a. Activation losses
    b. Bacterial metabolic losses
    c. Mass transport or concentration losses

The potential of the cell (or emf) can be calculated as:

$$E_{cell} = E_{emf} - (\sum \eta a + | \sum \eta c | + IR_{\Omega}) \quad (1.26)$$

Where,

$\sum \eta a$ – overpotential in the anode

$\sum \eta c$ - overpotential in the cathode

IR_{Ω} – internal or ohmic losses

Generally, the anode and cathode losses are included in the value of the OCV, like the theoretical value of the potential of the cell. So, we can rewrite the equation 1.26 like:

$$E_{cell} = OCV - IR_{int} \quad (1.27)$$

Where,

IR_{int} – internal or ohmic losses

So, with these two equations an MFC can be evaluated in terms of overpotentials and ohmic losses (equation 1.26) or with OCV and internal losses (equation 1.27).

1.5.3.2 - Ohmic losses

We say that we have an ohmic loss when the flow of electrons is hampered by the resistance of the electrode material. The nature of this losses involves resistance in both flow of electrons through the anode to the cathode or the flow of ions like ammonium or protons through the CEM. To overcome these problems there are, at least, three solutions: bring the electrodes closer together that would ease the flow of electrons, as would reduce the resistivity of the CEM or even, if none of the others is possible there is the possibility of increasing the solution conductivity [31]. With this last approach it is noteworthy to remind that the conductivity has a limit value that bacteria cultures can tolerate [27].

Activation losses

The reactions of oxidation and reduction require an energy called activation energy. These losses are bound to the transfer of electrons from or to a compound reacting on the electrode surface. This compound can be found either as a mediator in the surface of the bacteria or in the cathode as the electron acceptor. The smaller the current, the bigger the loss by activation. With a bigger current the loss tends to increase but at a lower rate. Logan, 2006 presents some solutions to minimize these losses, like: increase of surface area (since it improves the electrode catalysis) increase the operating temperature and the use of a bacterial biofilm on the electrode (increase bacteria concentration) [27].

Bacterial losses

The metabolic energy is generated when the electrons produced by bacterial activity from the substrate degradation, at low potential, to the electron acceptor, the anode, at high potential. If the difference between the substrate potential and anode potential is very low the bacteria will have less energy at their disposable and the MFC voltage is bigger. So, this is the best way to prevent this kind of losses. However, a difference too big would lead to the possible fermentation process by bacteria, enhancing their energy and reducing MFC voltage. There as to be an equilibrium value that is low enough to favor the MFC voltage but not so low as to favor the fermentation [27].

Concentration losses

Concentration losses are due to the transport mass of a species from or to the electrode that obstacles redox reactions and limits current production. The diffusion of chemicals species to the electrode surface is limited and this leads to a bigger loss when higher currents densities are being used. At the anode these losses can be caused by the poor release of oxidized species from the electrode surface, or by a poor quantity of reduced species provided. This involves an increase of the oxidized/reduced species ratio on the electrode surface, that can increase the electrode potential. The opposite could be verified on the cathode, determining a cathodic voltage decrease [27].

1.5.4 - Performance of MFC

Different parameters can be used to evaluate MFC efficiencies. Particularly, in wastewater treatments, important parameters are:

- Organic loading rate (OLR kg m^{-3} d^{-1}): the quantity of organic substance (expressed as COD, chemical oxygen demand) that is fed to an MFC, normalized by the net volume of the anode chamber and by the time (days)
- Effluent quality (kg m^{-3}): the concentration of organic matter (COD) discharged from the anode chamber)
- The COD removal efficiency (Reff, %) given by the difference between the COD influent and the COD effluent, divided by the COD influent.

The COD is a measure that indicates how much oxygen is needed to chemically oxidize the substance in the sample. The measured COD gives important information about how much “fuel” was used, for electrical current (and here we talk about Coulombic Efficiency), or for biomass

(growth yield) and finally for competitive reactions with alternative electron acceptors (O, NO_3, SO_3) [27].

Since the MFC is an electricity producer, it is important to quantify its amount of power output, through equation 1.28 [27]:

$$P = IE_{cell} \tag{1.28}$$

Although the previous equation is correct, it isn't the most suitable when it comes to measuring the power output because the current (I) is usually determined through Ohm's Law and the potential (E_{cell}) is measured across a fixed external resistor [27]. So, with Ohm's Law ($I=E_{cell}/R_{ext}$) and voltage new way of measurement comes equation 1.29, as follows:

$$P = \frac{E_{cell}^2}{R_{ext}} \tag{1.29}$$

The information that can be taken from the power output has to be normalized to some specific parameter in study to make clearer the comparison with different systems. Usually it is normalized to the anode surface area because that's where the biological reaction occurs. So, if one is to normalize the power to the surface area, then equation 1.30 will be the best suited to determine the power density ($W.m^{-2}$) [27]:

$$P_{An} = \frac{E_{cell}^2}{A_{An}R_{ext}} \tag{1.30}$$

A_{An} – surface area (m^2)

There is still another way of calculating the power density and it is when we're considering size and costing of the reactors. This happens because in equation 1.30 we don't consider power generation limitations in the cathode or materials (granular shaped) that difficult the normalization regarding surface area [27] so as an alternative, the power is normalized to the reactor volume, as equation 1.31 indicates [27]:

$$P_{\nu=}\frac{E_{cell}^2}{\nu R_{ext}} \tag{1.31}$$

ν – reactor's volume (m^3)

Coulombic Efficiency

Coulombic efficiency is defined as "the ratio between the coulombs that flow from the substrate to the anode and the maximum coulombs possible, if all the substrate is used to produce current" [27].

Fedbatch mode

$$\in_{C_b} = \frac{M\int_0^{t_b} Idt}{Fbv_{An}\Delta COD} \tag{1.32}$$

Where,

M – molar mass of oxygen ($32\ g.mol^{-1}$);

t_b – time of the batch (s);

I – current (A);

F – Faraday's constant ($9.64853*10^4$ C/mol);

b – number of electrons exchanged per mole of oxygen;

v_{An} – volume of liquid in the anolyte (m^3);

ΔCOD – difference of COD between the time t_b.

continuous flow with current production at steady conditions

$$\in_{C_b} = \frac{MI}{FbqCOD} \tag{1.33}$$

Where,

q – flow rate in the influent (cubic units/s)

ΔCOD – difference between the COD in the influent and the effluent

Some of the factors that might reduce this efficiency are the existence of alternative electron acceptors in the medium or wastewater and diffusion of oxygen through the CEM. The alternative electron acceptors are not an issue as long as the anode potential remains attractive enough for the bacteria culture.

Growth yield

The growth yield is defined as the increase of biomass which results in the use of the incremental amount of substrate and is given by the equation 1.34, as follows [27]:

$$Y = \frac{X}{\Delta COD} \tag{1.34}$$

Where,

X – biomass (g COD) produced over time (t_b or hydraulic retention time)

High growth yield might lead to a reduced coulombic efficiency due to the migration of electrons to the increasing biomass instead of the external circuit. One of the advantages of using an MFC instead of aerobic process is that most of the energy is used to generate electrical current and this means that bacteria don't have a lot of energy to grow [26].

COD Balance

The total COD in a system is divided in three different fractions of removal. The fraction that is used for the biomass growth, Y , the one that is used for production of electricity, ϵ_c , and for last, the fraction that is removed by unknown processes, which is given by the following equation [27]:

$$\varphi = 1 - \epsilon_c - Y \tag{1.35}$$

Energy efficiency

An important parameter to understand MFC performance for making electricity is to evaluate the system in terms of energy recovery. The overall energetic efficiency in given by [27]:

$$\in_E = \frac{\int_0^t E_{cell} I dt}{\Delta H m_{added}} \quad (1.36)$$

Where:

E_{cell} – Energy of the cell (V)

I – current (A)

ΔH – heat of combustion ($J.mol^{-1}$)

m_{added} – amount (mol) of substrate added

This formula can only be used by synthetic wastewater since the enthalpy variation is known, the same cannot be said if we use real wastewater because it is impossible to know this parameter [27].

1.5.5 - Direct applications of MFC

Synthetic wastewater

This is the easiest substrate to control in terms of pH, conductivity and other parameters. Rodrigo *et al.* (2009) [32] ran two different experiments with different wastewaters but same organic pollutants (glucose and peptone) and same organic loading but different ratio of biodegradable substrate. The best performance was the one where there was a slower ratio of biodegradable substrate loading [33]. The explanation given was that the slower ratio allowed the formation of intermediates that favored electricity formation.

Kuntke *et al.* (2012), in a study about ammonia recovery by an MFC conclude that ammonium transport was independent of the ammonia concentration in the anode and that it increases with current density. Furthermore, besides the increase of current density with the increase of ammonium concentration it was also noticed that the anode potential also increased. We can still add the fact that with every increase in ammonium concentration the current density increases as well but after some time it stabilizes. So, in order to increase the current density, the ammonium concentration should be increased from time to time [34].

Ghangrekar, MM and Shinde, V.B., 2006 ran an experiment with a membrane-less MFC to test its effectiveness. It was a work of some importance because although MFC that use membranes are effective, the use of these MFCs would be more welcome in water treatments if they didn't have to use them at all due to economic savings. They tested this possibility using COD, BOD, nitrogen removal and electricity production potential using a graphite electrode, from a synthetic wastewater as evaluation parameters. The carbon source used was sucrose with a 300-450 mg/L concentration. The experiment had a COD and BOD removal of 90%, a maximum current of 6.73 $mW.m^{-2}$ and a maximum nitrogen removal of 57%, proving this technology to be successful and economic saving (since the materials for membranes are, in most cases, expensive) [35].

Urine

Urine is of great interest because it is the greatest source of nitrogen in wastewater, around 79% [36], although it only occupies a 1% (v/v) of the wastewater [34][37]. The work of Mobley and Hausinger (1989) showed that the nitrogen present in urine is usually in the form of urea. Urea can be broken in ammonia and carbamate by the enzyme urease. Carbamate can still be decomposed in ammonia and bicarbonate if it reacts with water.

Urine is also considered the ideal MFC substrate because it has a high ionic conductivity, excess buffer capacity and even allows the recovery of nutrients. It can also provide a source of organic matter for electricity generation [38]. Furthermore, it is known that high salt concentration implies high ion conductivity. Urine is particularly rich in salt which means that, as a substrate, it has a high ion conductivity making it a suitable substrate for electricity production [38].

Kuntke *et al*, (2012) conclude that comparing real urine and synthetic wastewater and their performance when using the same MFC and base technology, real urine had a higher rate of ammonium transport. Although, it also concludes that the growth of unwanted bacterial culture reduced the coulombic efficiency. At the time it was offered a way to overcome this issue: lower the retention time.

In the same study, [34] was shown that, until 4 g/L, the ammonium concentration could be increased without any side effects on the bacteria performance since they were able to adapt to new and more concentrated compounds. Zhang et al. (2012) found some limitations on the influent medium, like for example the ammonium concentration, which can be risen until 4 g/L. After this limit concentration, the study observed that the MFC had worse performances or even near to zero [26]. On the other hand, Gyldemin *et al.* (2015) found an increase in current densities by increasing ammonium concentration to 5.1 g/l ($N\text{-}NH_4$) [39].

Swine wastewater

The population growth leads to an increase of the bovines and swine population. Both have a large amount of residues associated with their growth and care. All of these residues have a significant nutrients concentration that can be recovered instead of discharged. Swine wastewater has already been tested as a substrate in MFC systems [40][41].

Kim et al, (2008) used swine wastewater as feed for two different MFC equipments. The first consisted in a single chamber with the cathode exposed to air and the other in a two chambered MFC. The first conclusion was that in both equipments ammonia losses were accelerated with electricity generation. In the anode chamber, these losses were due to the presence of physical or biological factors that benefit from the increase of electricity generation (biological nitrification and denitrification, for example) [41].

When using swine wastewater as substrate it is to be expected some losses of nitrogen. These can happen if there isn't a buffer to stabilize the value of pH thus preventing the volatilization of ammonia (effect of high values of pH). Also, the presence of oxygen in the cathode is directly linked to another kind of loss of nitrogen because it favors biological and physical removal mechanisms [41].

One great advantage of using swine wastewater [42] is that, besides having the potential of generating electricity, it already has the microorganisms inside to do so [42]. Also, as it was expected, like in a regular MFC, the key parameters to improve the performance were: distance of the electrodes, internal resistance (this depends highly on the electrode material) and the electron acceptor in the cathode chamber [42].

1.6 Microbial Electrolysis Cell (MEC)

The other BES, and the one that this thesis was mostly focused on, is the MEC. In this technology organic matter is oxidized just like in MFC, and produces CO_2, electrons and protons [43] . Because the reaction is not spontaneous it is required to add a small voltage to the working electrode, to allow the production of H_2 in the cathode (through the reduction of protons). Indeed, as a consequence of the electron flows, a migration of cations through the membrane occurs from the anolyte to the catholyte [39]. Initially, MECs were used to produce hydrogen but years after, they started being used to remove and recover ammonia.

It works in completely anaerobic conditions and promotes the growth of anaerobic bacteria. The system produces hydrogen instead of electricity (MFC) [28].

A potentiostat can be required either to fix a potential, and in this scenario we are working with a bioelectrochemical cell or to produce and apply a current, and in this case we are working with a electrochemical cell [39]. In our case, the potentiostat is being used for fixing the potential of the working electrode and apply a current although we were working with a electrochemical cell.

One difference between MEC and MFC is that since MEC works with complete anaerobic conditions, unlike the MFC, it does not require aeration or another source of oxygen (electron acceptor). The presence of oxygen where there is hydrogen could result in explosive mixtures [28].

There is a variety of reasons for MEC's birth, being one of them the fact that most of the hydrogen gas produced comes from fossil fuels, through reforming, pyrolysis or gasification, that release a great amount of CO_2 and contribute to climate change [44], and even though there is an amount that comes from renewable sources, its cost is very high and yields are as big as 73% [28]. There are some bacteria that through photosynthesis can ferment organic matter like starch and glucose to hydrogen but at some point they lack the necessary energy to break down other by-products, from fermentation, and continue producing hydrogen, so their yields is very low, around 4 mol of H_2 from 1 mol of glucose comparing to its stoichiometric potential of 12 mol H_2 from 1 mol of glucose [28][45]. Plus Fang *et al*, (2005) after some experiments discovered that this process from photosynthetic bacteria was not feasible because of the large surface area requirements. Fortunately, after some experiments, it was found, in 2005 [44], that if one takes the original design of an MFC but does not use oxygen as electron acceptor while applying a small voltage in the anode chamber (>0.2V) protons, electrons and carbon dioxide can be produced and through the reduction of protons, so can hydrogen [28] [44]. This current is necessary because microorganisms cannot oxidize the substrate by themselves [28].

Another reason for hydrogen production comes with the fact that it is a valuable energy source and worth investigating as an alternative for fossil fuels since its combustion releases only water [43]. Furthermore, hydrogen, as a molecule, contains the highest energy amount per unit of weight, among gaseous fuels, having 120 MJ/kg, leading against 44 MJ/kg for gasoline, 50 MJ/kg for methane and 26.8 MJ/kg for ethanol [44].

The reactions in the anode and cathode chambers, if acetate is used as substrate are, respectively, 1.37 and 1.38 [43]:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + 9H^+ + 8e^- \quad (1.37)$$

$$8e^- + 8H^+ \rightarrow 4H_2 \quad (1.38)$$

A schematic figure of a typical single-chamber MEC, using glucose as substrate, is shown in figure 1.5.:

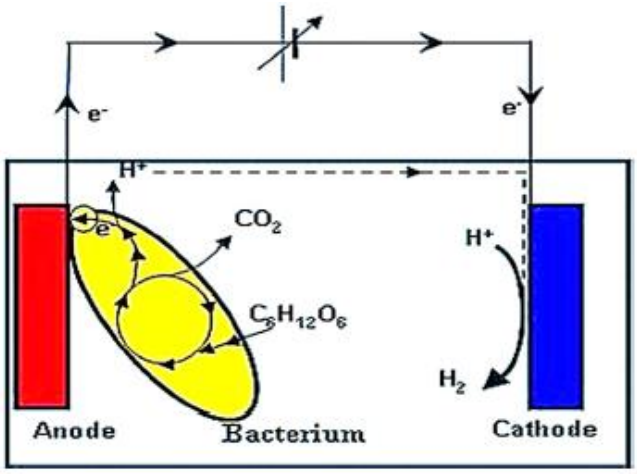

Figure 1. 5 - Example of a single chamber MEC [42]

A variety of substrates have been used in an MEC, which can be divided into 3 categories: wastewaters, fermentable and non-fermentable [46]. Some examples include swine wastewater, urine, brewery wastewater, etc [43].

1.6.1 Components

Anode

The materials used for the anode of an MEC are similar to those used in an MFC. These include carbon cloth [47], carbon paper [48], graphite granules [46], carbon felt[49], etc.

If one takes for example the use of graphite granules [28], a graphite rod is usually equiped, with it, as a current collector. Logan, 2008 [28], Kadier et al(2014) [43] and Cheng S.& Logan(2007) [45] used a pretreatment with high temperature ammonia for the anode material. This boosts the current generation and facilitates the fixation of microorganisms in the anode.

Cathode

The catalyst used in the cathode is mostly platinum since this material reduces the overpotential in this chamber. This overpotential is driven by the fact that the hydrogen evolution reaction is very low and tends to require high overpotentials for the hydrogen production [28].

Rozendal et al, (2008) tried to use a biocatalyst to prevent some disadvantages in the use of platinum such as high cost and poisoning by sulfide (substance commonly present in wastewaters). This biocathode consisted of a mixed culture of electrochemically active microorganisms. This biocathode was used for H_2 production and the effluent of this biocathode was used for another biocathode which produced a similar current density as that of a normal MEC using a platinum catalyst.

Membrane

The membrane has a similar function as the membrane in the MFC. Like the MFC, MEC does not necessarily need a membrane, being possible to work in a single chamber [35]. A two chamber MEC with membrane between the anode and cathode is more commonly used. This approach

prevents losses of hydrogen to microbes and mixing of hydrogen with CO_2 [28]. The first membranes used the same material as the MFC technology: Nafion or Fumasep FKE.

Kim et al, (2007) and Cheng&Logan, (2007) concluded that an anion exchange membrane (AEM) increased the MEC performances. An AEM allows the transport of anions across the membrane thus buffering the pH changes in both chambers of the system, diminishing the differences in its values [45][50].

Tubing and Gas Collection Systems

The small size of the molecule hydrogen makes it easy to lose in tubes that are not properly sealed. Logan, (2008) identifies Teflon and Viton as materials to minimize these losses, with small values for diffusivity (10^{-12} cm^2/s and 10^{-13} cm^2/s, respectively) [28].

Design

Like in an MFC system, the H-type is a possibility but it is subject to a high internal resistance caused by the large distance between the anode and cathode and small size of the membrane between them.

According to Logan, (2008) the cube shaped reactor with small distance between electrodes and an Anion Exchange Membrane (AEM) resulted in a high current density (288% of energy efficiency based on applied voltage, 0.6V) and achieved an increased hydrogen recovery (1.1 $m^3/(m^3$ of reactor per day)) [28].

MEC's with a single chamber reactor have the obvious advantages of having a less complex design and a lower capital cost associated when comparing to other cells.

As opposed to the regular MFC design, an MEC does not require a membrane because it works with complete anaerobic conditions so the flow of oxygen and mixture with H_2 is not a relevant factor [27]. Although the lack of a membrane means less ohmic resistances, there will still exist gradients of pH at the electrodes.

The main disadvantage of this design is the fact that the end product, hydrogen, is consumed by methanogens growing in the cathode or in the solution.

1.6.2 Thermodynamics of H_2 production

In order to have a spontaneous reaction, the variation of the Gibbs free energy has to be negative. However, when it comes to conversion of organic substrates to hydrogen, this variation is positive.

As it was referred earlier, the production of hydrogen is not spontaneous and a small voltage has to be applied in order to start the endothermic reaction of organic compound oxidation.

An example of the oxidation of acetate, a typical substrate for the MEC systems [28]:

$$CH_3COO^- + 4H_2O \rightarrow 2H^-CO_3 + H^+ + 4H_2 (\Delta G_r = +104.6 \frac{kJ}{mol}) \quad (1.39)$$

If we divide the value of the Gibbs free energy variation by the number of electrons involved in the reaction, multiplied by Faraday's constant, we have the minimum value of the voltage required to start the reaction [28]:

$$E_{eq} = -\frac{\Delta G_r}{nF} \quad (1.40)$$

Where,

E_{eq} – equilibrium voltage (V)

n – number of electrons involved in the reaction

F – Faraday's constant (96485 C)

The fact that the sign is negative means that we are dealing with a non spontaneous reaction.

If we use the equation 1.40 and apply to the case of the acetate, where we have 8 electrons involved, the equilibrium voltage would be -0.14 V

Like the MFC, this equilibrium voltage (V) can be calculated with the difference between the voltages of the separate electrodes [28]:

$$E_{eq} = E_{Cat} - E_{An} \quad (1.41)$$

The energy value of the anode can be calculated like in equation 1.21. The energy of the cathode can also be calculated with the equation 1.23, like in an MFC system, with the slight difference for the standard potential of the cathode and number of electrons involved [28]:

$$2H^+ + 2e^- \rightarrow H_2 \quad (1.42)$$

$$E_{cat} = -\frac{RT}{2F}\ln\left(\frac{p_{H_2}}{[H^+]^2}\right) \quad (1.43)$$

Where,

p_{H2} – partial pressure of hydrogen.

Equation 1.40 would, of course, lead to the same value as equation 1.41.

"The equilibrium voltage depends on hydrogen partial pressure and if we change it from 1 bar to 10 or 100 bar then the voltage given by the equation would be 0.03 or 0.06 V higher. This means that it is possible to produce hydrogen at pressures much higher than atmospheric" [28].

Like the MFC, the MEC is subject to some losses so the applied voltage should always be higher than the equilibrium voltage. Furthermore, like the MFC, the internal losses can be driven by anode, cathode and/or ohmic losses. Hence, the voltage can be obtained like [28]:

$$E_{ap} = E_{eq} - (\sum \varphi a + |\sum \varphi c| + IR_\Omega) \quad (1.44)$$

Where,

E_{ap} – applied energy in the cell (V)

E_{eq} – equilibrium energy of the cell (V).

Unlike the MFC, there is some energy that can be stored as chemical energy (hydrogen product). The energy that cannot be used is due to the losses inherent of the system: $E_{loss} = -(\sum \varphi a + |\sum \varphi c| + IR_\Omega)$ (1.44).

The higher the current, the higher the loss and for every increase in the applied voltage, the greater the electrical energy input per amount of hydrogen produced (Kwh/m^3 H_2). The real economic struggle here is to find the best applied voltage so that it can overcome overpotentials, produce a large amount of hydrogen but, at the same time not being so big as it would result in bigger losses as well [28].

Applied voltage in an MEC

There are two ways of applying a voltage to an MEC: power supply unit or potentiostat [28]. When using a power supply unit, a resistor is included to help calculate the current based on the voltage that crosses the resistor. This however results in a loss and this means that the voltage applied in the electrodes is actually lower than the one applied from the power source. This applied voltage can be calculated with the following equation [28]:

$$E_{ap} = E_{ps} - IR_{ext} \tag{1.45}$$

Where,

E_{ap} – applied voltage in an MEC;

E_{ps} – energy provided from the power source;

IR_{ext} – voltage that can be deduced substituting "I" with V/R_{ext}.

The other way is using a potentiostat. This device can either control the electrodes potential or set a specific current. Usually we use a potentiostat when studying the existence of a reaction at the anode or cathode [28].

Hydrogen Production Analysis

There are 3 ways of measuring the H_2 production, according to Logan et al, (2008), through 3 different equations [28].

Firstly, through equation 1.46 we have the mass balance equation to obtain the hydrogen production [28]:

$$V_{H_2,t} = V_{H_2,t-1} + x_{H_2,t}\left(V_{m,t} - V_{m,t-1}\right) + V_h\left(x_{H_2,t} - x_{H_2,t-1}\right) \tag{1.46}$$

Where,

$V_{H_2,t}\ and\ V_{H_2,t-1}$ – cumulative hydrogen gas volumes at current t and t-1 time intervals

$V_{m,t} - V_{m,t-1}$ – gas production during time interval

$x_{H_2,t} - x_{H_2,t-1}$ – fraction of H_2 gas in the current and previous intervals, respectively

V_m – volume of gas produced

V_h – volume of headspace.

Secondly, through equation 1.47 we have the production of hydrogen when using an anaerobic respirometer system or flowmeter [28]:

$$V_{H_2,t} = V_{H_2,t-1} + \left(V_{m,t} - V_{m,t-1}\right)\left(\frac{x_{H_2,t} + x_{H_2,t-1}}{2}\right) + V_h(x_{H_2,t} - x_{H_2,t-1}) \quad (1.47)$$

Thirdly,we can also collect all of the gas produced over a complete cycle (or a desired interval):

$$V_{H_2} = x_{H_2,h}V_h + x_{H_2,b}V_b \quad (1.48)$$

Where,

$x_{H_2,h}$ - mole fractions of hydrogen in the headspace

$x_{H_2,b}$ – mole fractions of hydrogen in the gas bag.

In equation 1.48 we assume that the volume for the gas bag is the volume of the gas measured by the respirometer.

There is still one correction to be made, in case we use a batch cycle, the tubing and the headspace need to be flushed with nitrogen gas. This nitrogen can enter in the gas bag causing a higher pressure. Also, in this case the volume of the bag is higher than the one measured.

$$f_{H_2,b} = \frac{x_{H_2.b}}{x_{H_2.b} + x_{C,b} + \cdots} \quad (1.49)$$

Where,

$x_{C,b}$ – moles of carbon dioxide

In this correction factor everything from carbon dioxide to even methane that are produced are held into account.

By using this correction factor, we now have, for the production of hydrogen when using a batch cycle [28]:

$$V_{H_2} = x_{H_2,h}V_h + f_{H_2,b}(V_m - V_{hl}) \quad (1.50)$$

Where,

$V_{hl} = (1\text{-}x_{N,h})V_h$ and $x_{N,h}$ is the molar fraction of N at the end of the sampling period in the headspace.

1.6.3 Performance of MEC

Hydrogen Yield

In order to evaluate the performance of the MEC, the amount of hydrogen produced has to be measured. This yield is calculated with equation 1.51 and is described as the moles of hydrogen produced from the moles of substrate consumed [28]:

$$Y_{H_2}\left[\frac{mol\ H_2}{mol\ S}\right] = \frac{V_{H_2}PM_s}{RT\Delta c_s} \quad (1.51)$$

Where,

P – atmospheric pressure measured in the laboratory (bar)

M_s – molar weight of the substrate ($g.mol^{-1}$)

Δc_s – substrate consumption over a set period of time

V_{H2} – volume of hydrogen (m^3).

Another way to determine the performance of the MEC, regarding the production of hydrogen, is using the COD variation over a set period of time and using the mass instead of moles [28]:

$$Y_{H_2}\ [\frac{g\ H_2}{g\ COD}] = \frac{V_{H_2} P M_{H_2}}{RT\Delta COD} \quad (1.52)$$

ΔCOD – COD consumption over a set period of time

Equation 1.52 gives us the ratio of total mass of H_2 produced from mass of substrate consumed. This equation is also more used for wastewaters and other complex substrates.

The last way of determine the yield is based on the moles of hydrogen produced (n_{H2}) and the theoretical maximum number of moles of hydrogen that could be produced (n_{th}) [28].

$$Y_{H_2} = \frac{n_{H_2}}{n_{th}} \quad (1.53)$$

$$n_{th} = n_s * st \quad (1.54)$$

Where,

n_s – moles of substrate converted;

st – stoichiometric production of hydrogen from 1 mol of substrate;

Another way to calculate this theoretical maximum number of moles of hydrogen is through equation 1.55 [28]:

We have 2ΔCOD because for each mole of COD removed, 2 moles of hydrogen are produced

$$n_{th} = \frac{2\Delta COD}{M_{O_2}} \quad (1.55)$$

Where,

M_{O2} – molar weight of oxygen (32 $g.mol^{-1}$)

2ΔCOD – production of hydrogen over a set period of time

After, with the measured current we can obtain the number of moles of hydrogen that could be recovered, based on measured current [28]:

$$\eta_{CE=} \frac{\int_0^t Idt}{2F} \tag{1.56}$$

When dividing η_{CE} by the η_{th} we obtain the Coulombic efficiency:

$$CE = \frac{\eta_{CE}}{\eta_{th}} \tag{1.57}$$

Now we have to consider the moles of hydrogen that are removed from the cathode chamber, η_{H2}, and the theoretical moles that would be produced from the measured current, n_{th}. With this ratio we can obtain the cathodic hydrogen recovery [28]:

$$r_{cat} = \frac{\eta_{H2}}{\eta_{CE}} \tag{1.58}$$

Finally, we can obtain the overall hydrogen recovery with equation 1.59 [28]:

$$r_{H_2} = CE * r_{cat} \tag{1.59}$$

If we convert this value to a percentage we have a clearer value of the performance of the MEC regarding the recovery of hydrogen.

The current efficiency (%) can also be calculated through the current determined with the nitrogen flux and the current measured [39].

The nitrogen flux, J_N (g N/(m^2*d)), can be calculated with equation 1.60 [28]:

$$J_N = \frac{\left(C_{An,in} - C_{An,out}\right) * Q}{A} \tag{1.60}$$

Where,

$C_{An,In}$ – Concentration of ammonia coming in the anode compartment (g N/L)

$C_{An,out}$ – Concentration of ammonia coming out of the anode compartment (g N/L)

Q – Anode flow rate (L/d)

A – Surface area of the membrane (m^2)

Then, with equation 1.61, we calculate the current density, A.m^{-2}, using the nitrogen flux [28]:

$$I_N = \frac{J_N * z_{NH4} * F}{M * 86400\ sd^{-1}} \tag{1.61}$$

Where,

J_N – nitrogen flux (g N/(m^2*d))

Z_{NH4} – charge of ammonium (1)

F – Faraday's constant (96485 C/mol))

M – molecular weight of nitrogen (14 $g.mol^{-1}$)

And finally with equation 1.62, we have current efficiency:

$$CE = \frac{I_N}{I_{Applied}} * 100 \quad (1.62)$$

Where,

$I_{Applied}$ – Measured current density (A/m^2)

Energy Yield

In order to determine this yield first we must compare the content of hydrogen to energy input regarding the electricity that can be obtained, the energy input in the substrate and finally in both the electricity and substrate [27].

This energy can be measured as the work energy released upon combustion.

The energy input into an MEC is considered to be 100% work (W) and is equivalent to Gibbs free energy. So, in order to calculate the energy yield relative to the electrical input, we have the work needed to produce hydrogen divided by the work regarding the energy input into the MEC [27].

$$\eta_E = \frac{-W_{H2}}{W_E} \quad (1.63)$$

We use equation 1.64 when we want to calculate the energy yield added by the substrate as follows:

$$\eta_S = \frac{W_{H_2}}{W_S} \quad (1.64)$$

Where,

W_{H2} – is the energy recovered based on Gibbs free energy regarding the production of hydrogen

W_S – is the amount of energy added by the substrate

W_s can be used by mutiplying the amount of moles of substrate consumed during a batch cycle (η_S) to the heat of combustion of the substrate (ΔH_s) or by multiplying it to the Gibbs free energy content of the substrate based on its oxidation by oxygen to bicarbonate and water (eq. 1.65).

$$W_S = \eta_S * \Delta G_S \quad (1.65)$$

The overall energy recovered based on both the electricity and substrate inputs can be calculated by the following equation [28]:

$$\eta_{E+S} = \frac{-W_{H_2}}{W_E - W_S} \quad (1.66)$$

In order to know how much each, power source and substrate, contribute to the total energy input we have [28]:

$$e_E = \frac{W_E}{W_E - W_S} \quad (1.67)$$

$$e_S = \frac{-W_S}{W_E - W_S} \quad (1.68)$$

From these equations we conclude that a higher applied voltage contributes to a larger amount of energy coming from the power source and lower from the substrate. In order to maximize the amount of renewable energy we should search to minimize as much as possible the energy input from the power source, W_E.

Current density

One of the main goals in engineering is to maximize the volumetric current density as much as possible. As it was already analyzed the greater the applied voltage the greater the current, however this voltage has a range that should be maintained. If the voltage exceeds 1V then the microbial electrolysis process will be replaced by the water electrolysis process and the system will not be working as it is supposed to. To have a normal function the voltage should be between the range of 0.4 and 0.8V [28].

Hydrogen Production Rates

The maximum volumetric production rate of hydrogen (m^3 H_2/m^3 of reactor per day) can be calculated through equation 1.69 [28]:

$$Q_{max} = \frac{I_v \left(\frac{A}{m^3}\right) r_{cat} [\frac{1C}{\frac{s}{A}}](0.5\ mol \frac{H_2}{mol})(86400 \frac{s}{d})}{F \left(9.65 * \frac{10^4\ C}{mol}\right) c_g (molH_2/L)(10^3 L/m^3)} \quad (1.69)$$

Once all the known values are discovered we obtain a much simpler version of equation 1.69:

$$Q_{max} = \frac{43.2 I_v r_{cat}}{F c_g(T)} \quad (1.70)$$

C_g – molar density of gas at standard conditions (T=298.15 K, P=1 bar)

I_v – average current volumetric density in a specific time period (A/m^3)

If the hydrogen is captured correctly then the r_{cat} tends to be 1 or close to 1, then the hydrogen production rate will depend only on the increase of the current [28].

1.6.4 Overall performance of MEC technology

This technology is very promising when it comes to wastewater treatments. First, it generates hydrogen as a product, with very high yields, reduce solid production and, in doing so, the cost of handling sludge automatically decreases, and lastly, because they are a closed circuit, this propriety limits the release of odors.

There is still the economical point of view of the use of the MEC: in order to be cost-effective there must be a sufficient amount of hydrogen produced to compensate the cost of the applied voltage.

However, real wastewaters reveal some problems that result in low production of hydrogen such as: slow degradation of complex substrates and low conductivities. These reasons also contribute to a low and inefficient current density.

The interest in developing clean and renewable hydrogen comes from, but not only:

- Substitution of fossil fuels in petrochemical industries [27, 42];
- Food industry (saturation of fat and oils) [28],
- Metal industry (reducing agent for metallic ores) [28].

The great advantage about hydrogen is that it can respond to all these demands using renewable substrates like biomass and wastewater.

Besides the general cost-effective issue, there are others that need a development in order to increase the overall performance of this technology. Some of them include [28]:

- Better performance regarding the use of complex substrates like polymeric and particulate feedstock
- Change of present cathodes to bio or chemical ones that are not platinum based
- Dismiss of the membrane to eliminate pH gradients
- Eliminate methanogenic consumption of the hydrogen product
- Develop a scalable MEC that can be cost-effective

1.6.5 MEC Direct Applications

Urine

In the work of Kuntke *et al*, (2014) a two chamber MEC was used with titanium and platinum, no stripping existed and a CEM membrane (Nafion) was also used, separating the electrodes. This set up was able to produce hydrogen and recover ammonium. The ammonium removal ranged from 27 and 34% in the batch cycles of different experiments, being higher in diluted urine.The work showed that high cathodic efficiencies were achieved proving most the ammonium was being well recovered from the cathode chamber. Also, high coulombic efficiencies were observed meaning that most of the available oxidizable organic material was used for current generation [37].

When comparing with the previous work of Jeremiasse et al, (2010) it was possible to conclude the viability of urine as a plausible feedstock for MEC since the results of Kuntke, 2014 and Jeremiasse et al, (2010) were similar with the first having a H_2 production of 50.8 $m^3/(m^3$ of reactor*d) and the second with 50 $m^3/(m^3$ of reactor*d) and current productions of 24 A/m^2 and 22.8 A/m^2, for Kuntke, (2014) and Jeremiasse et al, (2010), respectively [37].

The biggest issue was the durability of this good performance since the equipment was not working with the same performance after a short period of time (few days to one week). In order to overcome this problem, it was suggested to change the catholyte with some regularity with the only consequence of a lower current density [37].

The fact that no stripping column was used led to a difficult scenario when trying to take the hydrogen from the catholyte. Furthermore, it was also shown that the inherent issue with

diffusion/migration of cations led to a low percentage of ammonium and this resulted in a difficult recovery in the cathode. As a solution, an effective NH_3 stripping system and the conversion of chemical energy to electrical energy to facilitate the migration of ammonium ions were offered.

When comparing the performance of an MEC and MFC in the ammonia removal and current density, we see that an MEC bests an MFC. Jeremiasse et al, (2011) obtained 22.8 A/m^2 produced whereas Kuntke, (2012) shows low densities such as 5.5 A/m^2 when using an MFC. Furthermore, ammonia removal efficiencies in the MEC were also greater (up to 34%) than the ones obtained with an MFC (30%) [33, 36].

Swine wastewater

As it was explained in the previous chapter, swine wastewater has nutrients like ammonia and phosphorous that can be recovered but it also has the potential to produce hydrogen. In the work of Kadier et al, 2014, swine wastewater is described has a promising feed stream for H_2 production [43].

The issue involved include lack of carbon for feeding the organisms and the deviation of production of methane instead of hydrogen. Furthermore, it is also mentioned that the technology MEC using one chamber faces difficulties regarding the recovery of hydrogen gas, at the cathode [43].

Conventional swine wastewater treatments include anaerobic lagoons, constructed wetlands and storage with landspreading, which come with production of odors, emissions of methane, nitrous oxide and ammonia, proliferation of pathogens and deterioration of the systems due to nitrogen accumulation [51]. Besides the hazardous on the natural environment, these treatments processes are also costly. However, since H_2 is a valuable product, its production through MECs can help balancing this expensive process, since hydrogen can recover three times the energy than the one that it is applied for its operation [45]. In the work of Logan, (2009) using a single chamber MEC, hydrogen productions of 0.9-1 $m^3/(m^3*d)$ were achieved at an applied voltage of 0.5V. Also, coulombic efficiencies, or fraction of electrons used to produce hydrogen, were up to 70%. Some issues that the experience endured were loss of hydrogen to methanogens present in the wastewater that contributed to lower percentages of recovery (17-28%) [51]. However, this technology was found to be promising but depends on the materials used and energy needed, in order to be cost effective [51].

1.7 Motivation and thesis outline

As it was described in this chapter, contamination of soils, water bodies and atmosphere with an excess amount of nutrients leads to environmental and even human risks like eutrophication and a variety of cancers and other human hazards. Also, the plants can't use all of the fertilizer which means that its key component, ammonia, is lost in the soil and lower water levels. Moreover, the Haber-Bosch process consumes a very high amount of energy, when producing ammonia. These two issues cause a great economic impact. The removal and recovery of ammonia from wastewaters, using bioelectrochemical systems, is presented as possible solution to all these issues. In this work, two-chamber MECs were used and its efficiencies in removing and recovering ammonia were determined. In chapter 1, a state of art was presented indicating different types of BES, including possible configurations and materials for the several components. In chapter 2, the different materials used in the experience are described as are the methods. Chapter 3 will present the results and a brief discussion of the MECs' performance. Conclusions and future work are presented in chapter 4.

2

Materials and Methods

2.1 Set-up and operation of the MEC

Two MECs were used in this thesis, MEC1 and MEC 2. Both were kept in a room at a fixed temperature, 25°C. Both cells are made of transparent polycarbonate in a two-chamber device (anode and cathode chamber, both with approximately 130 mL). Between the two chambers a membrane is present, for exchange of cations (CMI-7000. Membrane International Inc.) with an area of approximately 64 cm^2. In this set-up the anode chamber contains the anolyte (synthetic at first and then real wastewater) while in the cathode chamber is found the catholyte (0.1M saline solution of sodium chloride).

Figure 2. 1 - Set-up of the MEC1 (on the left) and MEC2 (on the right)

The anode of the MEC1 was composed of a conductive sheet in a carbon felt (AlfaAesar, thickness of 1.12 cm and 99.9% purity) attached to a stainless-steel mesh working as a current collector. Regarding the MEC2, the anode chamber was filled up to 2/3 of its volume with graphite granules (d<2 mm, David snc) working as anode. Also, a reference electrode can be found in

both anode chambers (Ag/AgCl, mod. MF2052) for measuring the anode's potential. Furthermore, the anode, cathode and reference electrode are linked to a multichannel potentiostat (Thasar, mod. Ivium-n-Stat) for the application of a fixed potential to the anode and for the control of the process.

A graphite bar (AlfaAesar) was immersed in the middle of the granules and had the same function of the stainless-steel mesh, as a current collector. Both cathodes were made of a stainless-steel mesh.

Figure 2. 2 - Picture of the anodic chamber of the MEC1 (A -using carbon felt) and MEC2 (B - using graphite granules) [52]

The anode chamber is fed from three different entering points. This allows a better homogeneity of the wastewater minimizing, in the process, "deadzones". A peristaltic pump (Watson Marlow, mod. 120 U) was used to feed the anolyte. The anolyte has also 2 exit points, one of them leads back to the anolyte as a recirculation point, using another peristaltic pump (Watson Marlow, mod. 505S), while the other is from where we can collect the effluent.

Linked to the cathode chamber we can find a stripping column and then an absorption column. Both these columns are filled with raschig rings (Carlo Erba, LxA 4x4 mm). These rings were invented by Friedrich Raschig, they have equal diameter and length, and have the function of packing the column in order to facilitate mass transfer operations making the separation process much easier [53]. The columns are connected to a compressor (KNF, mod. N86) responsible for the air insufflation. This compressor provides aeration and works in intermittent mode with 30 minutes intervals.

The stripping column is filled with the catholyte solution previously described. This solution is then recirculated back to the catholyte chamber with a peristaltic pump (Velp, modello SP311). The stripping column is accompanied by a digital probe (Mettler Toledo, mod. INPRO 3253I) connected to a transmitter (Mettler Toledo, mod. M300) to measure the pH.

The absorption column contains 1L of sulfuric acid solution (1M), H_2SO_4 with the purpose of trapping the ammonia coming from the stripping column.

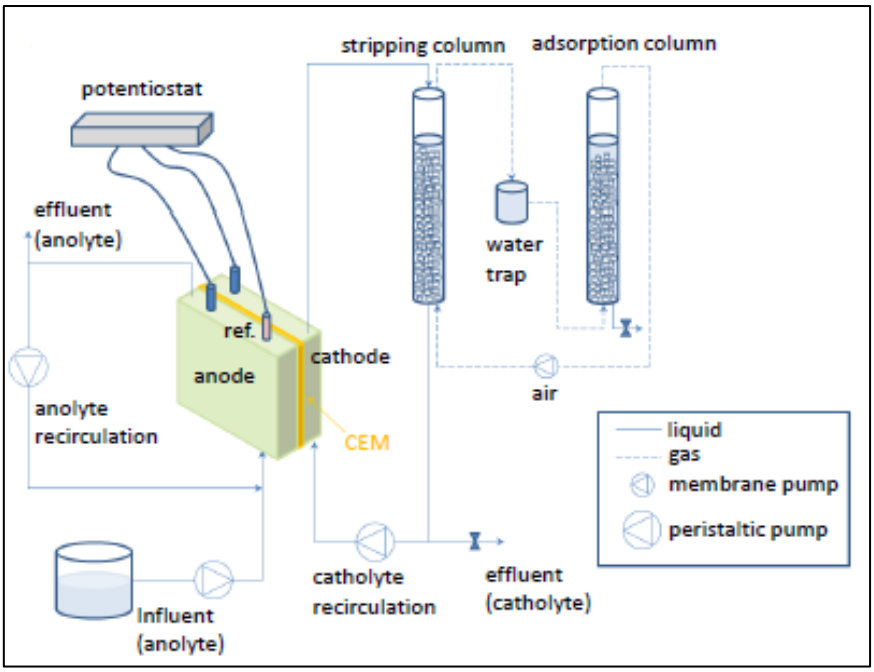

Figure 2. 3 - Animated scheme of the set-up of an MEC. ("Effects of different anodes and operating conditions on ammonium recovery by microbial electrolysis cells (MEC) Milia S., Erby G., Carucci A.")

Figure 2. 4 - Final set-up of MEC1 with stripping column (1), water trap (2), absorption column (3), recirculation (4) and peristaltic pump (5)

2.2 Cells feed

The MEC1 and MEC2 worked with both synthetic wastewater and real wastewater. The synthetic wastewater was prepared by modifying its ammonia concentration from 1 g/L to 2.5 g/L for the MEC1 before it was changed to real wastewater. The MEC2 worked with synthetic water with a constant concentration of 2.5 g/L, since the initial period of acclimation was already done before this experimental period. Parameters like hydraulic retention time and flow were changed regularly. Once the real waste wastewater started being used at first there was no additional of NH_4HCO_3 or NH_4Cl like in the synthetic wastewater. The synthetic wastewater composition can be found in table 2.1 with all the specific reagents. In tables 2.2 and 2.3 we can find a detail composition of both the vitamin complex and trace elements, respectively, that were added to synthetic wastewater.

As it was mentioned before, the hydraulic retention time and ammonium concentration were changed and as they changed so did the phase that it was being worked on. In table 2.4 and 2.5 it is found a detailed description of these two parameters and also the flows that were used in the different phases, in MEC1 and MEC2, including the real wastewater used as substrate.

Table 2. 1 - Composition of the synthetic influent that fed the cell, during the experiment

Reagent	Concentration (g/l)
NH_4HCO_3	4.80÷11.29
KCl	0.74
NaCl	0.58
KH_2PO_4	1.36
K_2HPO_4	1.74
NH_4Cl	0.56÷1.91
$MgSO_4*7H_2O$	0.10
$CaCl_2*2H_2O$	0.07
$CH_3COONa*3H_2O$	3.32÷4.98
Trace elements	0.1
Vitamin complex	1

Table 2. 2 - Composition of the trace elements

Reagent	Concentration (g/l)
$FeCl_2*4H_2O$	2
H_3BO_3	0.05
$ZnCl_2$	0.05
$CuCl_2$	0.03
$MnCl_2*4H_2O$	0.5
$(NH_{4)6}MO_7O_{24}*4H_2O$	0.05
$AlCl_3$	0.05
$CoCl_2*6H_2O$	0.05
$NiCl_2$	0.05
EDTA	0.5
HCl	1

Table 2. 3 - Composition of the vitamin complex

Reagent	Concentration (g/l)
Biotin	0.004
Folic acid	0.004
Pyridoxine hydrochloride	0.02
Riboflavin	0.01
Thiamine hydrochloride	0.01
Nicotinic acid	0.01
DL-calcium pantothenate	0.01
B12 vitamin	0.0002
p-aminobenzoic acid	0.01
Lipoic acid (thioctic)	0.01
Myo-inositol	0.01
Choline chloride	0.01
Niacinamide	0.01
Pyridoxal hydrochloride	0.01
Sodium ascorbate	0.01

Table 2. 4 - Operation conditions for each phase of the experiment, for MEC1

Phase	Type of wastewater	Phase duration (days)	Concentration $N\text{-}NH_4^+$ (mg/l)	Concentration CH_3COONa (mg/l)	Feed flow (ml/min)	HRT(h)
I	Synthetic	10	1000	3000	0.18	12
II	Synthetic	7	1500	3000	0.18	12
III	Synthetic	7	2000	3000	0.18	12
IV	Synthetic	11	2500	3000	0.18	12
V	Synthetic	18	2500	3000	0.26	8
VI	Synthetic	28	2500	3000	0.36	6
VII	Real	50	2800	2000	0.36	6

Table 2. 5 - Operation conditions for each phase of the experiment, for MEC2

Phase	Type of wastewater	Phase duration (days)	Concentration $N\text{-}NH_4^+$ (mg/l)	Concentration CH_3COONa (mg/l)	Feed flow (ml/min)	HRT(h)
I	Synthetic	18	2500	3000	0.18	12
II	Synthetic	9	2500	3000	0.26	8
III	Synthetic	27	2500	3000	0.36	6
IV	Real	32	1009	3000	0.18	12
V	Real	35	2271	2000	0.18	12

2.3 Inoculum

The inoculum for the anode consists of two sources:

1. an active sludge that comes from a wastewater treatment plant located in Cagliari (Is Arenas). In this plant there is a pre-nitrification and nitrification treatment and the nitrogen concentration that the bacteria are subjected to does not exceed 25 mg ($N\text{-}NH_4^+$)/L.
2. the same real wastewater that will be treated, an anaerobic sludge coming from an anaerobic digester for the treatment of agroindustrial wastes located in Guspini, Sardegna

2.4 Analysis methods

The analysis in this experiment were performed to know the efficiencies of the nitrogen removal, biomass consumption within the cell and also the ability to generate current. Regarding the nitrogen removal regular measures were made to the anolyte influent and effluent, catholyte and absorption column to know the concentration of ammonium nitrogen ($N\text{-}NH_4^+$). The sodium acetate was also monitored but only for the anolyte influent and effluent. The conductivity and pH were continuously monitored since these parameters can indicate the normal and good performance of the cell. The pH was measured with the aid of a pH-metro GLP22-Crison and the conductivity with a digital multimeter Hach, HQ30d model.

The anolyte influent and effluent of both MEC1 and MEC2 were both centrifugated, however, depending on the type of substrate, synthetic wastewater or real wastewater, these samples were centrifugated at different speeds and time. When working with synthetic wastewater the samples (anolyte influent and effluent) were subject to a centrifugation of 4000 rpm for 15 minutes. After the change to real wastewater, the samples had to be centrifugated at higher speeds like 10 000, 15 000 and even 20 000 rpm, for times of 15 or, sometimes, 20 minutes.

After centrifugation, the samples were filtrated with cellulose acetate filters (Sartorius ø 25 mm, ø 0.45 µm). Only after this centrifugation the sample could be diluted with distillate water for the analysis of ammonium concentration and deionized water for the acetate and total organic carbon analysis.

The ammonia nitrogen concentration was obtained via spectrophotometry with the aid of Nesselr's reagent using a visible range absorption spectrophotometer (HITACHI, model U-2000, figure 2.5), with a wave length of 420 nm.

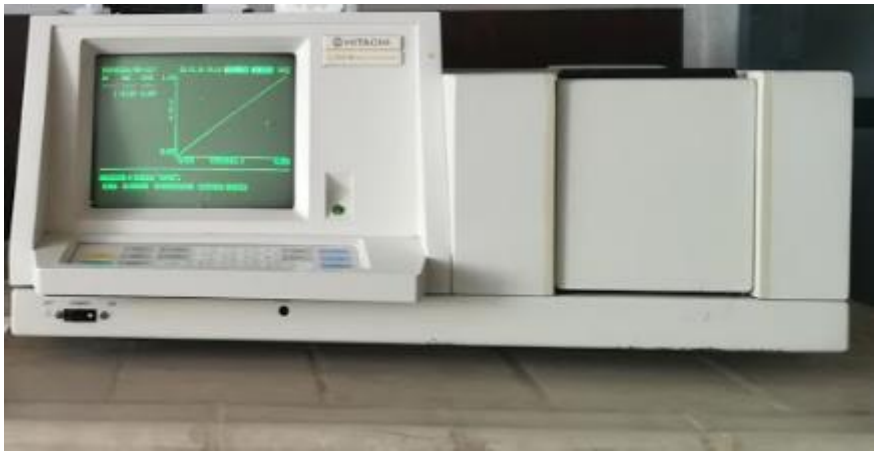

Figure 2. 5 – Spectrophotometer HITACHI, model U-2000

The acetate was measured using a HPLC model P680 (DIONEX), with an absorption lamp ranged within the visible and ultraviolet wave length (DIONEX, mod. UVD170U), shown in figure 2.6. The equipment is linked to a software called *Chromeleon* (Peak Net® 6), that shows a cromatogram after the analysis where one can see the concentration of acetate of the sample analyzed.

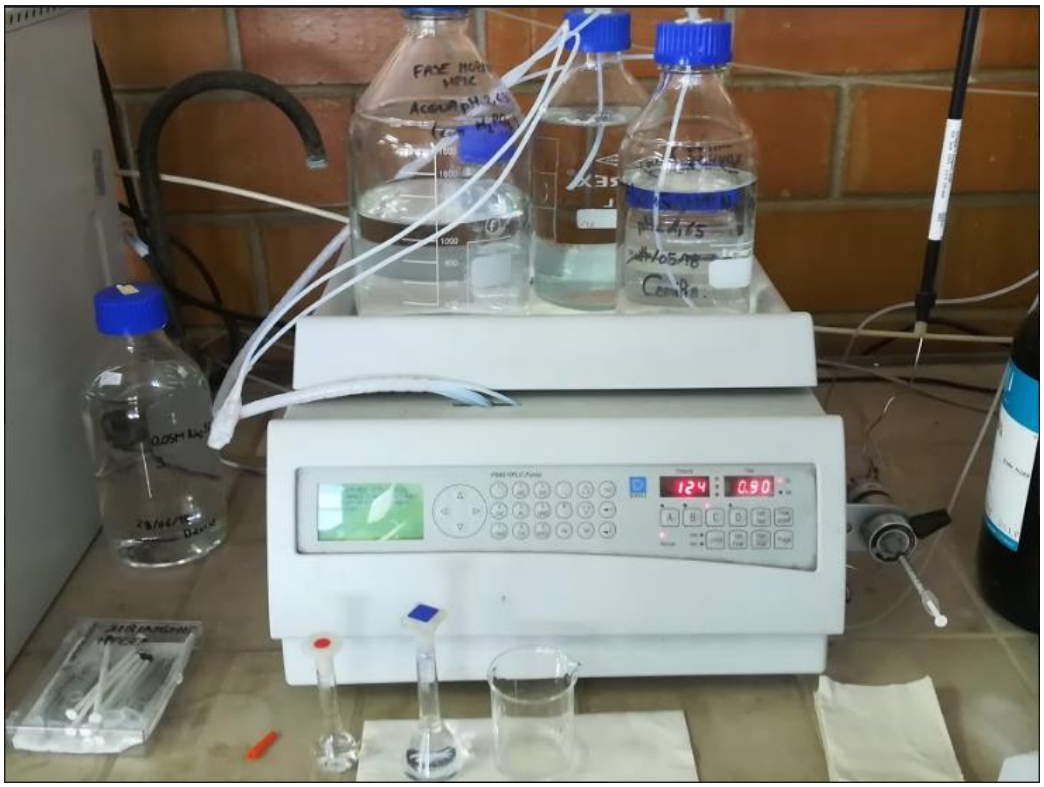

Figure 2. 6 - HPLC model P680 (DIONEX)

The electric behaviour was monitored through a potentiostat (Thasar, model IVIUM-n-STAT), figure 2.7. The potentiostat was activated, using a special software (Ivium), in chronoamperometric mode setting a fixed potential at the anode, which acts as a working electrode, equal to -200 mV compared to the reference electrode (Ag / AgCl), while the cathode acts as a counterelectrode. The software Ivium provides as a result of the chronoamperometry, a graph that represents the trend of the current measured over time.

While working in chronoamperometric mode, other tests were conducted in open circuit (OCV) to check the performance of the cell in the absence of a potential in the anode. The test consists in disconnecting the electrical supply to the anode and cathode while the cell continues to be normally supplied. The performance of the cell and the progress under conditions of OCV were evaluated with routine analysis of collected samples.

Figure 2. 7 - Potentiostat IVIUMnSTAT

The potentiostat allowed to perform 2 more tests: linear scanning voltammetry (LSV) and cyclic voltammetry (CV), besides the chronoamperometric tests. For the first test (LSV), the cells need to be in OCV conditions, meaning that 2 hours before the test, cell anode and cathode were electrically disconnected so that the system could stabilize in these conditions. For the LSV tests, there was no interruption in the feed, that worked with a potential of 0.1 mV/s vs Ag/AgCl. This LSV test gave the polarization and power curve that will be found, for this experiment, in chapter 3.

The test CV can be done in *turnover* and *non-turnover* mode, depending on the presence or absence of substrate, respectively [54]. In order to arrive to *non-turnover* mode, 36h before the test, the feed source is stopped and the potential is fixed and applied to the working electrode (WE) (-200 mV vs Ag/AgCl). During the test, the potential was changed between -0.8 and 0 V vs Ag/AgCl, at a speed of 1 mV/s and the results were registed through a voltamogramm. As it was explained before, the *turnover* mode needs the substrate so for this to happen, the feed source is stopped only a little before the execution of the test. The scan velocity and time intervals for this test were the same as in the *non-turnover* mode test.

2.5 Data analysis

2.5.1 Nitrogen recovery

With the ammonia concentration in the anolyte influent and effluent we can, through equation 2.1 obtain the removal efficiency (%):

$$RE\ (\%) = \frac{C_{An,inf} - C_{An,eff}}{C_{An,inf}} * 100 \qquad (2.1)$$

Where,

$C_{An,\ inf}$ – Concentration of $N\text{-}NH_4^+$ in the anolyte influent ($mg.L^{-1}$)

$C_{An,\ eff}$ – Concentration of $N\text{-}NH_4^+$ in the anolyte effluent ($mg.L^{-1}$)

The flow of nitrogen crossing the cation exchange membrane was calculated with equation 2.2:

$$J_N = \frac{(C_{An,inf} - C_{An,eff}).Q}{A_m} \quad (2.2)$$

Where,

J_N – flow of N-NH_4^+ going through the membrane ($g.m^{-2}.d^{-1}$)

Q – flow of the anolyte influent ($l.d^{-1}$)

A_m – surface area (m^2)

$C_{An,\ inf}$ – Concentration of N-NH_4^+ in the anolyte influent ($g.L^{-1}$)

$C_{An,\ eff}$ – Concentration of N-NH_4^+ in the anolyte effluent ($g.L^{-1}$)

The maximum theoretical flow of nitrogen crossing the membrane is calculated according to the applied current, as shown:

$$J_{N,max} = \frac{j.z_{NH_4^+}.M.86400\ (sd^{-1})}{F} \quad (2.3)$$

Where,

$J_{N,max}$ - maximum flow of N-NH_4^+ crossing the membrane ($gm^{-2}d^{-1}$)

j - measured current, expressed as a current density (Am^{-2})

$z_{N\text{-}NH4+}$ - charge of the ammonia nitrogen (-)

M - molecular weight of the nitrogen (14 $gmol^{-1}$)

F – Faraday's constant (96485 $Cmol^{-1}$)

The maximum daily absorption capacity of the sulfuric acid, H_2SO_4, within the absorption column was obtained with the following equation:

$$C_{abs,H2SO4} = \frac{J_{N,max}.\frac{C_{An,inf}}{M}.A_m.t}{\frac{2}{V}} \quad (2.4)$$

Where,

$C_{abs,\ H2SO4}$ - maximum absorption capacity of the column ($mol.l^{-1}$)

$C_{an,\ inf}$ - concentration of the N-NH_4^+ in the anolyte influent ($mol.l^{-1}$)

t – operation time (d)

A_m – membrane surface (m^2)

M – molecular weight of nitrogen (14 $gmol^{-1}$)

V – absorbent solution volume (L)

The stripping efficiency SE (%) was calculated with the following equation:

$$SE = \frac{C_{An,inf} - C_{An,eff} - C_{cat}}{C_{An,Inf}} . 100 \quad (2.5)$$

Where,

$C_{An,inf}$ – concentration of $N\text{-}NH_4^+$ in the anolyte influent ($g.L^{-1}$)

$C_{An,\ eff}$ – concentration of $N\text{-}NH_4^+$ in the anolyte effluent ($g.L^{-1}$)

C_{cat} – concentration of $N\text{-}NH_4^+$ in the catholyte ($g.L^{-1}$)

Lastly, it was determined the daily recover of $N\text{-}NH_4^+$ ($R_{N\text{-}NH4+}$, $gm^{-2}d^{-1}$) in the absorption column, normalized to the membrane surface described as follows:

$$R_{N-NH_4^+} = \frac{C_{col,abs}}{A_m . t} \quad (2.6)$$

Where,

$C_{col,abs}$ – concentration of $N\text{-}NH_4^+$ in the absorption column ($g.L^{-1}$)

A_m – membrane surface (m^2)

t – operation time (d)

2.5.2 Electric parameters

The potentiostat measures a current and then converts to a current density j (Am^{-2}) with the following equation:

$$j = \frac{I}{A_{an}} \quad (2.7)$$

Where,

I – produced current (A)

A_{an} – projection of the surface of the anodic surface (m^2)

The coulombic efficiency was obtained with an equation, indicated in Sleutels et al. (2009), that uses the current that can be theoretically produced with the quantity of organic substrate that is consumed, as described in the following equation [55]:

$$I_{th} = nFQ\left(C_{inf} - C_{eff}\right) \quad (2.8)$$

Where,

I_{th} – theoretically produced current from the consumed organic substance (A)

n – released moles of electrons per mole of consumed organic substance

F – Faraday's constant (96485 $Cmol^{-1}$)

Q – influent's flow ($L.s^{-1}$)

C_{inf} – Concentration of the influent organic substance (mol. L^{-1})

C_{eff} – Concentration of the effluent organic substance (mol. L^{-1})

The coulombic efficiency (%) was therefore determined with the formula:

$$CE = \frac{\int_0^t I_m dt}{I_{th} t} * 100 \quad (2.9)$$

Where,

CE – coulombic efficiency (%)

I_m – measured current (A)

I_{th} – theoretically produced current from the consumed organic substance (A)

t – chosen time interval (d)

The coulombic efficiency was also calculated with a formula delivered by the work of Gildemyn et al. (2015), expressed as the ratio between the nitrogen flow as a current density (I_N, expressed in A m^{-2}) and the measured current density, j (A m^{-2}), obtained from equation 2.7 [39]:

$$CE = \frac{I_N}{j} * 100 \quad (2.10)$$

The nitrogen flow, I_N, can be determined by equation 2.11:

$$I_N = \frac{J_N . z_{NH_4^+} . F}{M . 86400(sd^{-1})} \quad (2.11)$$

Where,

J_N – nitrogen flow going through the membrane (eq. 2.2)

$Z_{N\text{-}NH4+}$ - nitrogen charge (-)

F – Faraday's constant ($Cmol^{-1}$)

M – molecular weight of nitrogen ($gmol^{-1}$)

Finally, in order to know the amount of energy to provide the cell so that the nitrogen crossing the membrane can be extracted, equation 2.12 was used:

$$E_N = \frac{j . A_m . \Delta V . \frac{24}{1000}}{(C_{An,inf} - C_{An,eff}) . Q} \quad (2.12)$$

Where,

j – current density (Am^{-2})

A_m – membrane surface (m^2)

ΔV – potential difference between anode and cathode (V)

$C_{an,inf}$ – $N\text{-}NH_4^+$ concentration in the anolyte influent ($g.l^{-1}$)

$C_{an,\ eff}$ – $N\text{-}NH_4^+$ concentration in the anolyte effluent ($g.l^{-1}$)

Q – flow of the anolyte influent ($l.d^{-1}$)

3

Results and discussion

3.1 Introduction

In this chapter a detailed data analysis of the samples analyzed during the experimental period is reported. Particularly, the impacts of different ammonia concentrations and hydraulic retention times are investigated, found in each phase of the experiment, and the overall performance of the MECs. For this evaluation, the ammonia recovery rate and removal rate, the acetate removal efficiency and other parameters are considered to determine which MEC was the one with the best performance.

Since two kinds of water were used (synthetic and real) they will be separated in 2 different sub-chapters for a clearer understanding of the behaviours of the different materials that compose the anode in MEC1 and MEC2 working with two different substrates.

3.2 Synthetic wastewater (SWW)

3.2.1 Nitrogen recovery

The flux of nitrogen (in the form of ammonium) that crosses the membrane, J_N, is defined as the amount of nitrogen that crosses the membrane, from the anodic chamber to the cathodic chamber, daily, per surface area of the membrane. This makes this same nitrogen available for recover. In the following figure 3.1 J_N values are shown, in red, for MEC1, while in blue the ammonia removal efficiency from the anolyte is shown.

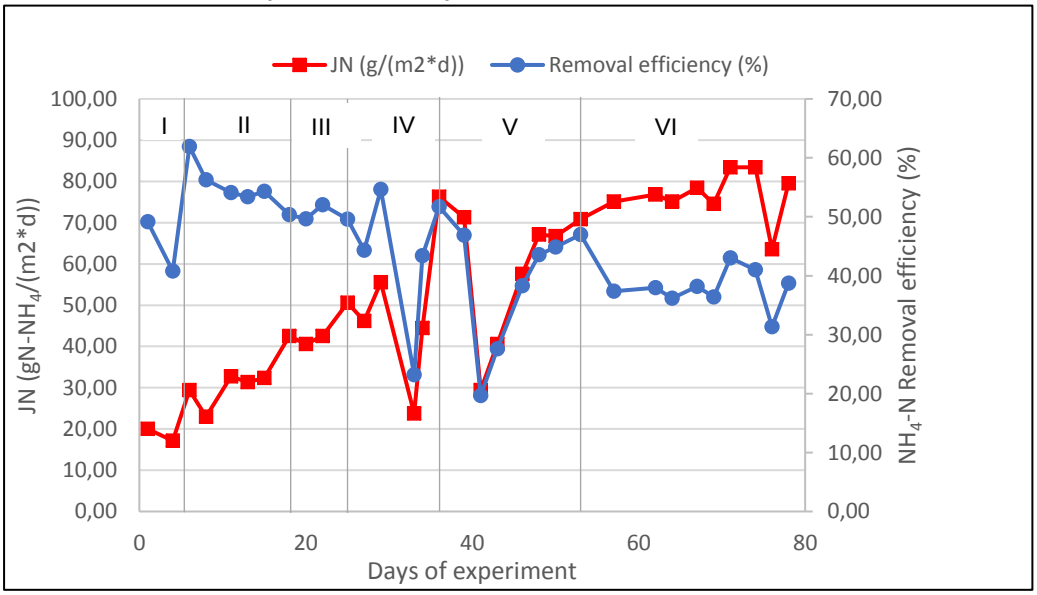

Figure 3. 1 - Removal efficiency and daily nitrogen flux that crosses the membrane, treating synthetic wastewater, for the MEC1

As it is seen in the graph, from phase 1 to phase 6, with the increase of ammonia concentration (from 1 to 2.5 g/l) the NH_4^+-N removal efficiency decreases slightly and progressively during the various phases, while J_N increases going from phase 1 to phase 6. This can be explained by the increase in the ammonia concentration in the medium, from phase 1 until phase 4, while the hydraulic retention time was changed from phase 4 to Phase 6 (from 12 h to 6). So, the greater the concentration in the medium, the greater was the mass of ammonia recovered, but lower the removal efficiency. The maximum value of the removal efficiency was obtained in the first phase and was 61.92%, with an HRT of 12h, whereas the maximum number of grams recovered was in the last phase, VI, with a value of 83.43 g $N\text{-}NH_4$/(d*m^2membrane), with a HRT of 6h. The two major drops that can be observed in the graph, in phases 4 and 5, are probably due to a malfunction of the feeding pump, that contributed to a strong decrease in the ammonia removal rate and J_N. After some days the anodic biomass of the MEC1 was able to achieve similar values to those before the malfunctioning, increasing again the ammonia removal rate. Since the ammonia concentration was the same, the parameter that was responsible for the performance of the MEC1 was the HRT. A decrease of the HRT (and accordingly an increase in the influent flow) led to higher J_N. Higher retention times lead to higher removal efficiency, but lower J_N. These are the reasons why it is possible to see a continuous growth in the red line from phase 5 to phase 6 (where the HRT changed from 8 h to 6 h) and a drop in the blue line.

One can conclude, from figure 3.1, that the amount of nitrogen recovered in the cathodic chamber is directly linked to the quantity of nitrogen that crosses the membrane. The greater the flux, the greater the amount recovered.

Until phase 4, a maximum value of 1.37 g/L and 55.53 g/(d*m^2) are found regarding the nitrogen removed from the anolyte and the nitrogen flow, respectively. After the malfunction, it can be found a value of 1.17 g/L and 83.43 g/(d*m^2), also for the nitrogen removed and nitrogen flow, respectively.

The same type of study was done for the MEC2 and the behaviour can be found in the figure 3.2. In this figure, we have the same red and blue line describing the amount of grams of nitrogen crossing the membrane, daily, per membrane area and removal efficiency, in percentage, respectively.

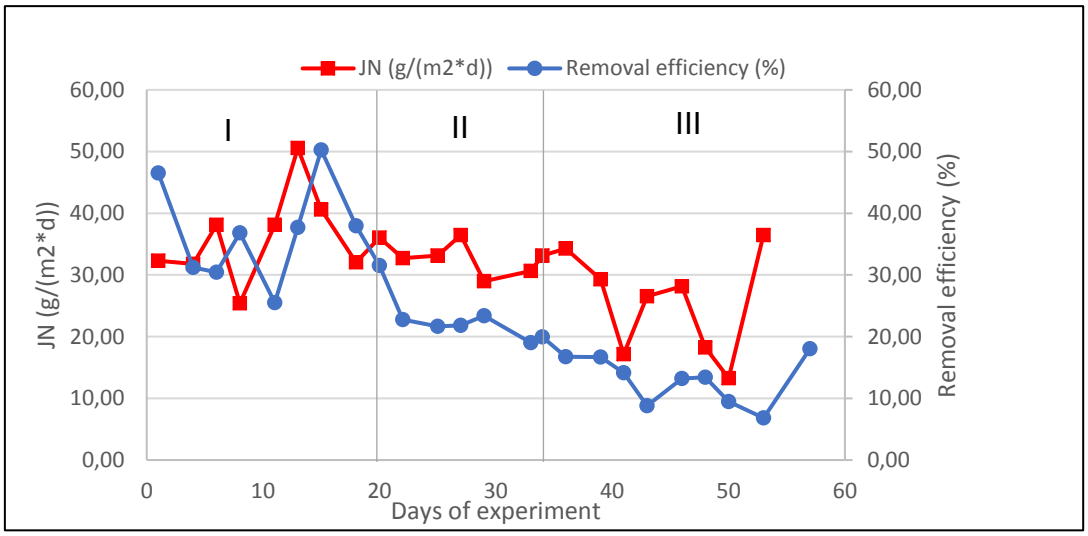

Figure 3. 2 - Removal efficiency and daily nitrogen flux that crosses the membrane, treating synthetic wastewater, for the MEC2

A different behaviour can be seen from the MEC2. The decrease in the HRT did not lead to an increase in J_N, this because the decrease of the HRT (and so, the increase in the influent flow) led to a sensible decrease of the removal efficiency compared to the MEC1, thus to a high decrease also in the ammonia flux from the anode to the cathode. The greater removal efficiency, 50.27% can be found in the first phase, where the HRT was greater and equal to 8h and the bigger amount of nitrogen removed, 59 g $N\text{-}NH_4/(d*m^2$ membrane) was in the first phase as well.

The greater values for nitrogen removed from the anolyte and the nitrogen flow were 1.25 g/L of nitrogen and 59 g $N\text{-}NH_4/(d*m^2$ membrane), respectively.

The maximum theoretical value for the flow of nitrogen that crossed the membrane, daily was also calculated. The equation used is found in chapter 2, as equation 2.3. Then a ratio was made between the nitrogen flow crossing the membrane that was measured and the theoretical maximum value, $J_N/J_{N,max}$ that gave the information about how close were the equipments working in comparison with its maximum possible value. Furthermore, the stripping efficiency (SE), in percentage was also calculated and compared to both J_N and the ratio $J_N/J_{N,max}$. These 3 parameters are found in table 3.1 and table 3.2, for MEC1 and MEC2, respectively.

In these two tables it can be observed that MEC1 has 0.7 and 60.6% as its maximum ratio between J_N and $J_{N,max}$ and stripping efficiency, respectively whereas, for MEC2 it shows 0.9 and 48.9% for those same parameters.

In average, MEC1 has 53.19 g/m^2 daily amount of nitrogen, and if one considers only the last phase where the concentration of ammonia was 2.5 g/L, the average is even higher, reaching 76.67 g/L.

The MEC2 has a value of 32.19 g/m^2 nitrogen recovered, also on a daily basis. The absorption column showed an average efficiency of 81% throughout the experiment, for MEC1 (SWW), 90%, for MEC2 (SWW) and MEC1 (RWW) and 37% for MEC2 (RWW). Both results come to show the efficacy of this system in the recovery of nitrogen.

Table 3. 1 - Parameters regarding the nitrogen recovery, for MEC1, using synthetic wastewater

Day	JN, max g/m2.d	JN/JN,max	SE (%)
4	53.87	0.3	40.8
6	43.88	0.7	60.6
8	48.44	0.5	56.3
11	61.82	0.5	49.6
13	56.10	0.6	52.2
15	65.54	0.5	54.3
18	68.23	0.6	48.2
20	68.27	0.6	46.5
22	75.22	0.6	52.0
25	86.31	0.6	49.6
27	91.24	0.5	44.3
29	87.62	0.6	54.6
46	97.73	0.6	38.3
48	103.80	0.6	43.4
50	111.64	0.6	44.7
118	110.83	0.7	38.2
120	108.70	0.7	36.4
122	115.69	0.7	43.0

Table 3. 2 - Parameters regarding the nitrogen recovery, for MEC2, using synthetic wastewater

Day	JN, max g/m2*d	JN/JN,max	SE (%)
4	66.33	0.5	31.2
6	58.63	0.5	30.4
8	62.13	0.6	35.2
11	49.03	0.5	25.5
13	43.35	0.9	37.4
15	70.19	0.7	48.9
25	54.24	0.6	21.6
27	46.15	0.7	21.7
29	45.33	0.8	23.4
46	34.24	0.8	13.2
50	21.18	0.9	9.5

In table 3.3 it can be seen, for each cell, the removal efficiency and the nitrogen flow through the membrane, daily. The values in red represent the highest nitrogen recovery rates and the ones in bold, the values with the same concentration of ammonia in the influent but different hydraulic retention times (HRT). The anode chambers of the MEC1 and MEC2 were equipped with different types of materials. The MEC1 had a carbon felt, while the MEC2 had graphite granules. This difference poses a significant factor considering both the nitrogen flux from the membrane and the recovery efficiency. As it can be seen from the table, different behaviours for the two MECs are evident, since that an HRT decrease in the MEC1 led to a slight decrease in ammonia removal %, this decrease is compensated by higher Jn and then higher ammonia recovery rates. For MEC2 the significant decrease in ammonia removal efficiency conducts to a lower Jn and ammonia recovery rate as well. In blue we can see the higher values of the removal efficiency. Here we conclude that the higher recovery and removal rates are in MEC1, with the lowest HRT.

Table 3. 3 - Removal efficiency and nitrogen flow through the membrane, for both cells, for every phase

Phases	MEC1				Phases	MEC2			
	N-NH4 influent conc.	HRT	RE	JN		N-NH4 influent conc.	HRT	RE	JN
	(mg/L)	(h)	(%)	g/(d*m2)		(mg/L)	(h)	(%)	g/(d*m2)
I	1000	12	52.0±9.1	22.4±5.3	I	**2500**	**8**	**35.2±7.5**	**36.1±7.6**
II	1500	12	53.9±0.5	32.1±0.7	II	**2500**	**6**	**21.4±1.7**	**33.0±2.9**
III	2000	12	50.7±1.2	41.9±1.1	III	**2500**	**4**	**14.8±6.7**	**29.7±13.3**
IV	**2500**	**12**	**43.0±11.9**	**44.1±12.1**					
V	**2500**	**8**	**39.9±10.9**	**60.0±16.6**					
VI	**2500**	**6**	**37.8±3.3**	**76.7±6.0**					

The results found in table 3.3 show great promise when compared to those in literature. In the work of Desloover et al, (2012), when working with optimal conditions and an ammonium nitrogen concentration of 5 g/L, removal efficiencies were as high as 50% and the nitrogen crossing the membrane was 120 $g.m^{-2}.d^{-1}$. This last result is considerably higher than the maximums obtained for MEC1 and MEC2, during the experiments with 83 $g.m^{-2}.d^{-1}$ for the first and 60 $g.m^{-2}.d^{-1}$ for the second (however, the experiment had twice as much ammonia as the one conducted in this thesis' experiment). In the study of Sotres et al, (2015) the nitrogen crossing the membrane was 25 $g.m^{-2}.d^{-1}$. In this experiment the $N\text{-}NH_4^+$ concentration was 900 mg/L and given the fact that the system was provided with further ammonium in a rate of 7.4 $g.l^{-1}.d^{-1}$ and COD, at a rate of 10.7 $g.l^{-1}.d^{-1}$ the results obtained, in MEC1 and MEC2 are considered promising and not far from other results obtained in past experiments [40].

3.2.2 Consumption of Acetate

In figure 3.3 we see the evolution of the acetate consumption (%) regarding MEC1, and its removal (g/L). The progression is more or less the same except in the first part, in phases 1 and 2, where we see a higher percentage of acetate consumed, for lower amounts of acetate removed. In the first three phases there was a concentration of 2 g/L in the anolyte. When the

ammonia concentration changed to 2.5 g/L, the acetate concentration was increased to 3 g/L. The lower concentration led to bigger values in consumption since the bacteria deplete 70% of the influent acetate. After that, the consumption and removal of acetate stayed with a similar evolution over time. The major drops in the acetate consumption have a correspondence with the MEC malfunction, as it was explained before. Most of the acetate consumption values are between 40 and 50%, whereas the acetate removed is mostly between 1 and 1.5 g/L. This shows that in most cases, the bacteria are not using all the acetate available and an increase in its concentration would not lead to a bigger consumption or performance.

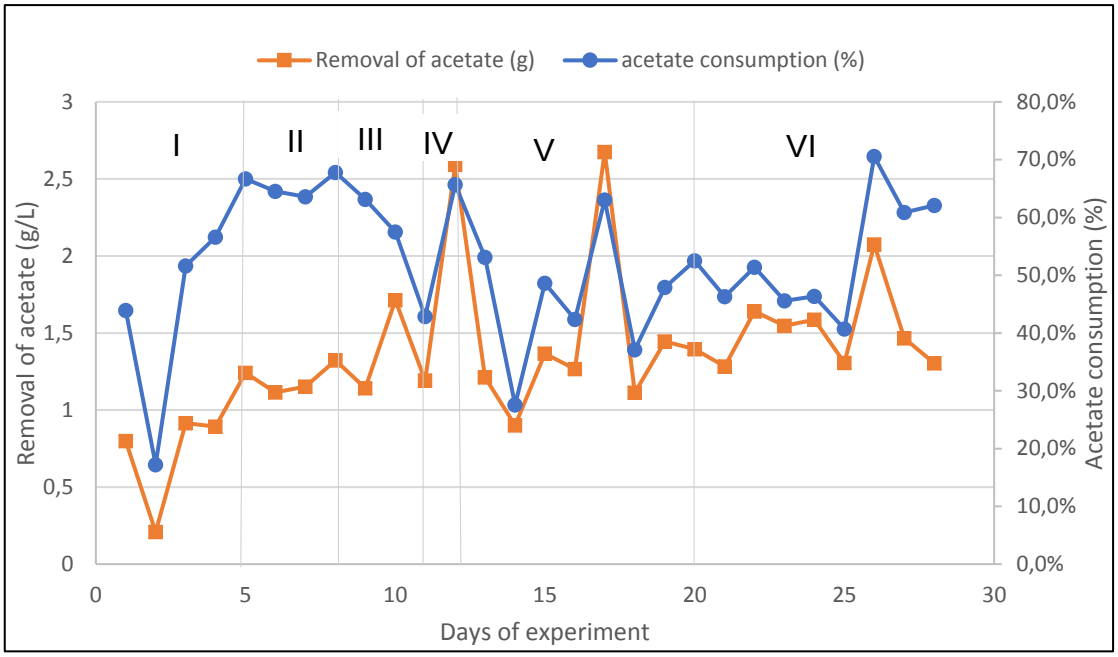

Figure 3. 3 - Acetate consumption, in MEC1

In MEC2, the acetate consumption and its removal shows a similar behaviour throughout the experiment (figure 3.4). We can confirm this since the highest value for removal efficiency was in the second phase with a value of 57.6% and it was in a phase where the acetate concentration in the medium was 3 g/L. Besides this value, the acetate consumption never rose above the value of 60% and most of the amounts of acetate removal were lower than 1.5 g/L. A decrease trend can be seen from phase 2 to phase 3, accordingly to worst performance in MEC2 at this time.

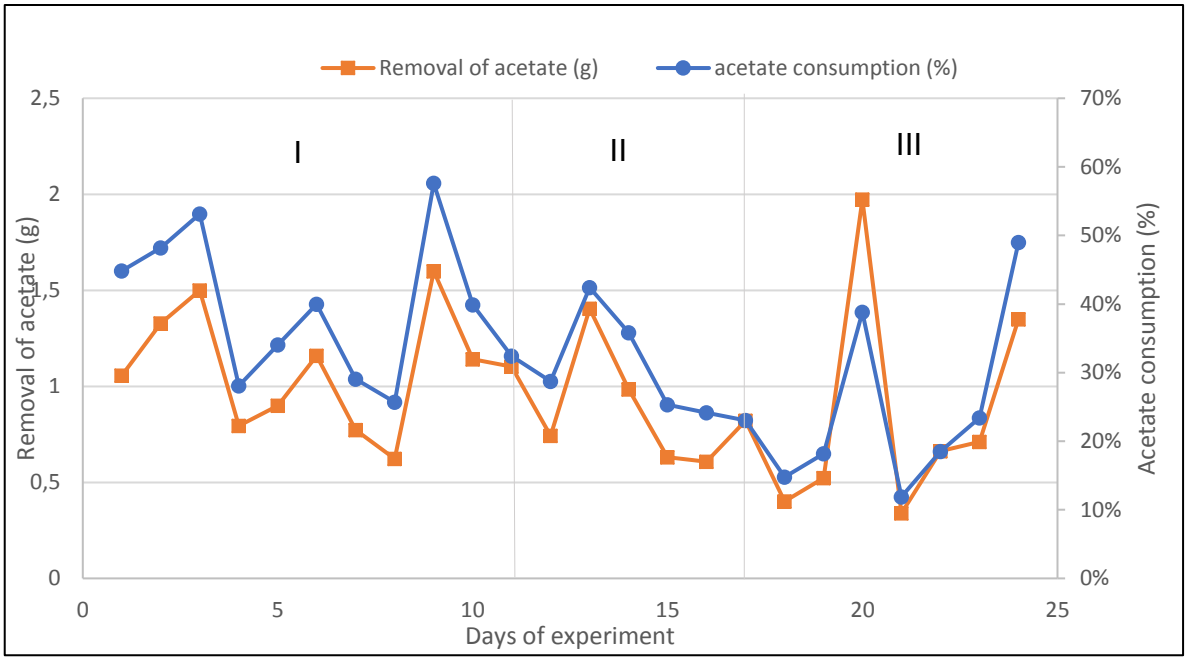

Figure 3. 4 - Acetate consumption, in MEC2

3.2.3 Electric performance

In the figure 3.5, it is shown the current evolution during chronoamperometry test for the MEC1. As one can see, there are some drops in the current density progression. Those are linked to malfunctions of the system since, at steady conditions, it is to be expected an increase or stable current.

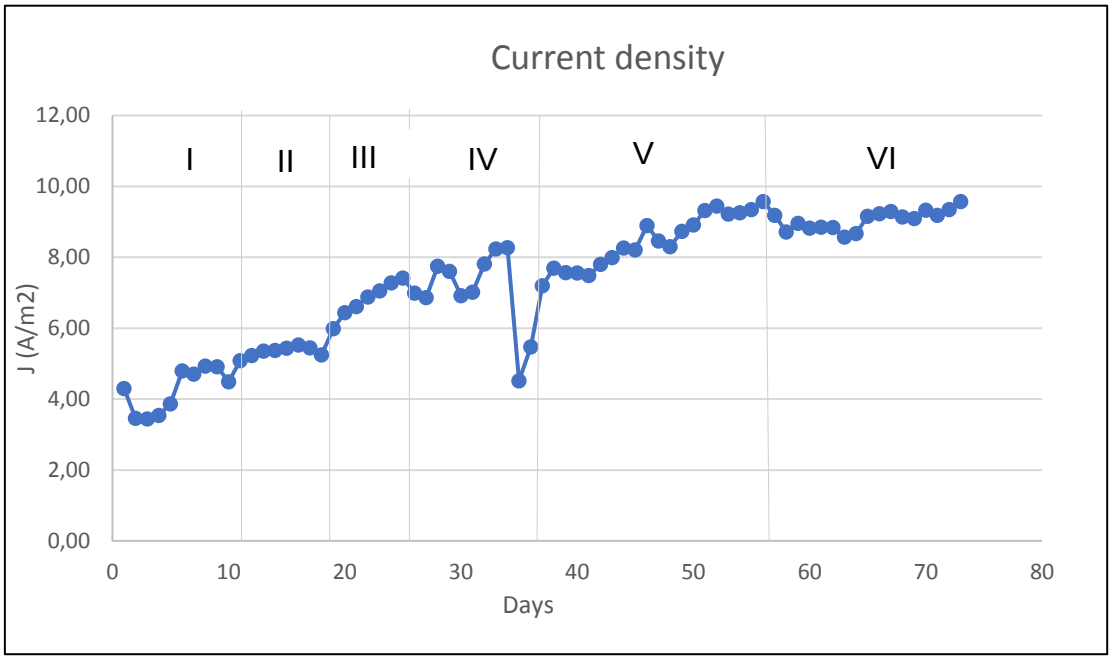

Figure 3. 5 - Current density progression, for the MEC 1

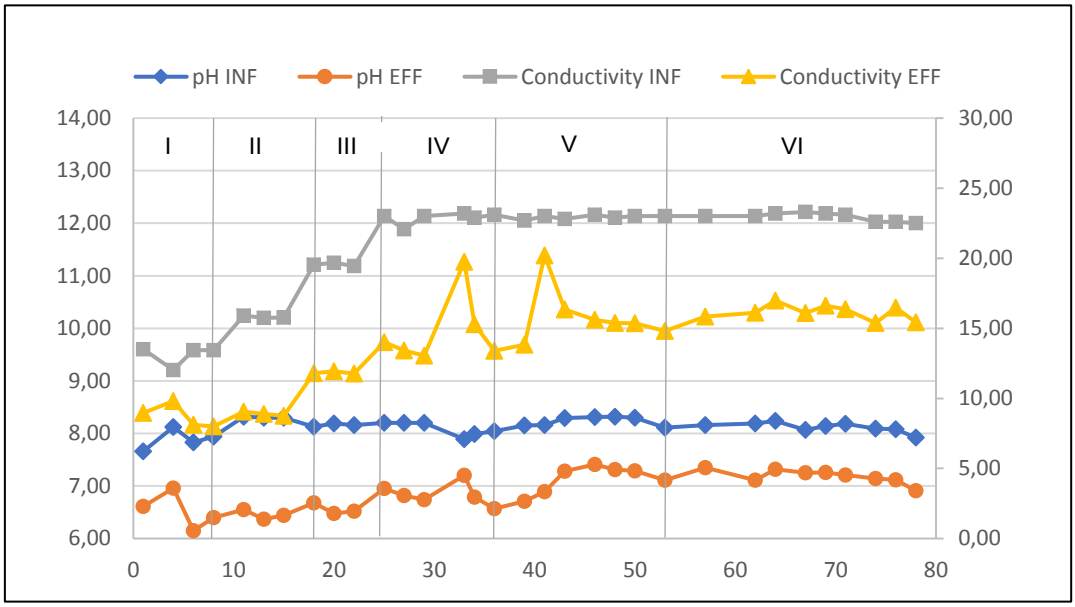

Figure 3. 6 - pH and conductivity, for MEC1. using synthetic wastewater

Figure 3.6 shows pH and conductivity values for influent and effluent SWW. As it is possible to see from figure 3.6 the effluent pH rises in the same days of the worst values founded for ammonia removal. This is probably related to a bacterial inhibition, since that bacteria produce H^+ and consume bicarbonates when degrading organic substance (in this case the acetate), causing a pH decrease. A similar behaviour can be seen for the effluent conductivity, where the lowest ammonia removal values are related to the higher conductivity values in the effluent.

Chronoamperometry was performed also for MEC 2, as shown in figure 3.7.

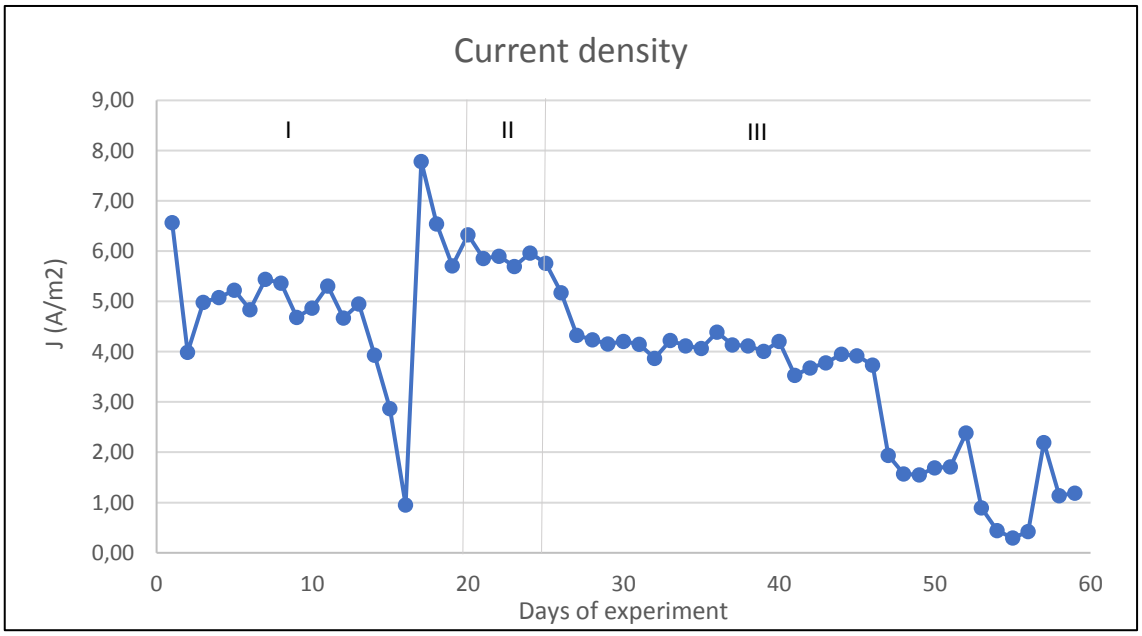

Figure 3. 7 - Progression of the current measured, for MEC 2

It is shown in the graph a big decrease of the current measured and after the steady behaviour until day 40, another, but not so drastic, decrease is also evident. This is in line with the decrease in performance for ammonia removal and acetate degradation during phase 3.

Figure 3.8 shows pH and conductivity for influent and effluent anolyte. pH trend was almost constant during the different phases. An increase of the effluent conductivity was observed in the same days of the smaller ammonia removal rates.

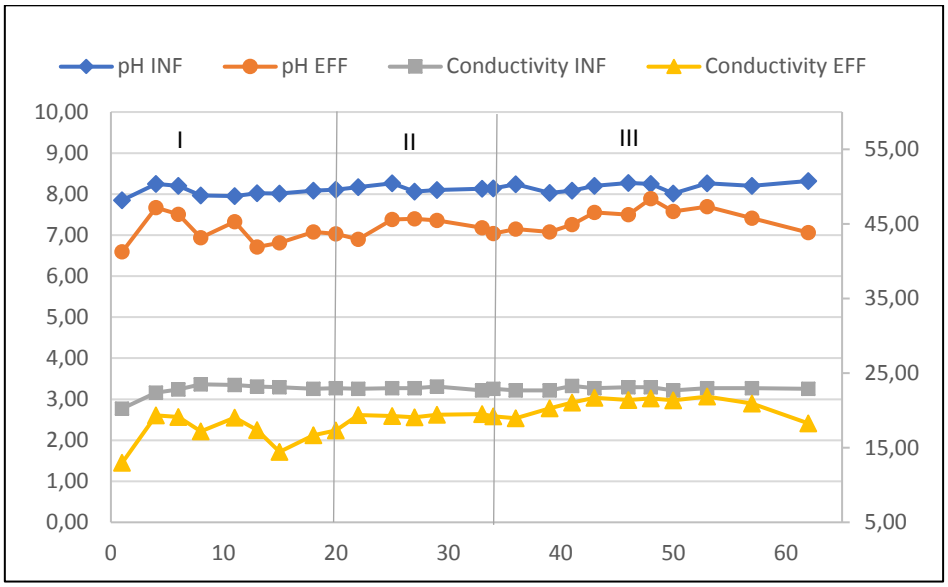

Figure 3. 8 - pH and conductivity, for MEC2

There is also a decrease in the acetate consumption rate of the bacteria around this period. After that and until day 20 we see an increase in the acetate consumption, correspondent to an increase in the current and pH and conductivity.

With the values of the chronoamperometry test was possible to obtain the values of current intensity (mA). With these values were then determined some control parameters such as current density (J), coulombic efficiency (CE%) and energy provided (E_N) for the ammonia extraction. The formulas that were used to calculate these parameters can be found in chapter 2, in the sub-chapter 2.5.2 (electric parameters). The values are found in the next two tables, 3.4 and 3.5, for MEC1 and MEC2, respectively.

Table 3. 4 - Values for the current density, coulombic efficiency and energy to give to the cell MEC1, using synthetic wastewater

Phase	J (A/m2)	CE (%)	EN (kWhkg/N)
I	4.4±0.6	40.4±5.7	7.4±0.9
II	5.3±0.2	48.5±2.5	6.1±0.3
III	6.2±0.8	54.7±8.6	5.5±0.8
IV	7.2±0.6	46.4±14.3	7.1±3.3
V	7.9±1.2	54.9±14.9	4.3±1.7
VI	9.2±0.3	66.7±5.3	3.7±0.3

Table 3. 5 - Values for the current density, coulombic efficiency and energy to give to the cell MEC2, using synthetic wastewater

Phase	J (A/m2)	CE (%)	EN (kWhkg/N)
I	5.2±1.2	52.5±16.1	4.7±1.6
II	5.1±0.9	52.7±9.1	4.9±0.8
III	3.1±1.1	61.8±14.8	3.5±1.4

The maximum values that MEC1's performance shows for current density, coulombic efficiency and energy are, respectively, 9.2 $A/m^{-2.}$ 66.7% and 7.4 $kWgkgN^{-1}$. MEC2, on the other hand, working more or less in the same way as MEC1 had 5.2 $A.m^{-2}$, 61.8% and 4.9 $kWhkgN^{-1}$ for the same parameters. MEC1 had higher values comparing to MEC2, showing better performances regarding conversion of substrate in electrons. However, regarding E_N, one would be interested in lower values since it means that the system is more self efficicient and there is less need for power input. Here it can be concluded that the lowest E_Ns were linked with higher concentrations of acetate, feedsource.

If one takes into account the literature values found in the paper of Desloover et al. (2012), in a study for the ammonia recovery with an electrochemical cell, the values obtained for the same 3 parameters are 10 $A.m^{-2}$, 34% and 11 $kWhkgN^{-1}$, but with an ammonia concentration of 5g/L, twice as much as the one used in this experiment.

The coulombic efficiency obtained in the work of Sotres et al, (2015) was as high as 56%, which was found in one single experiment, the others were ranged from 3 to 30%. The values in this thesis study were averaged above 40% in all phases [40].

3.2.3.1 Voltammetry performance

The analysis LSV (*Linear Sweep Voltammetry*) in the MEC1 cell generated a polarization curve and a power curve, for the anode and the cathode. In the following figure, figure 3.9, it is possible to see an example of the electrochemical method, in this particular case, for the anode of MEC1. It is possible to split the polarization curve in 3 regions. Each region is directly related to one of the three kinds of losses, explained in chapter 1. They are: activation losses, ohmic losses and finally concentration losses, in this order, as shown in the figure. The power curve gives the value of the maximum power density, which in this case is approximately 150 mW/cm^2.

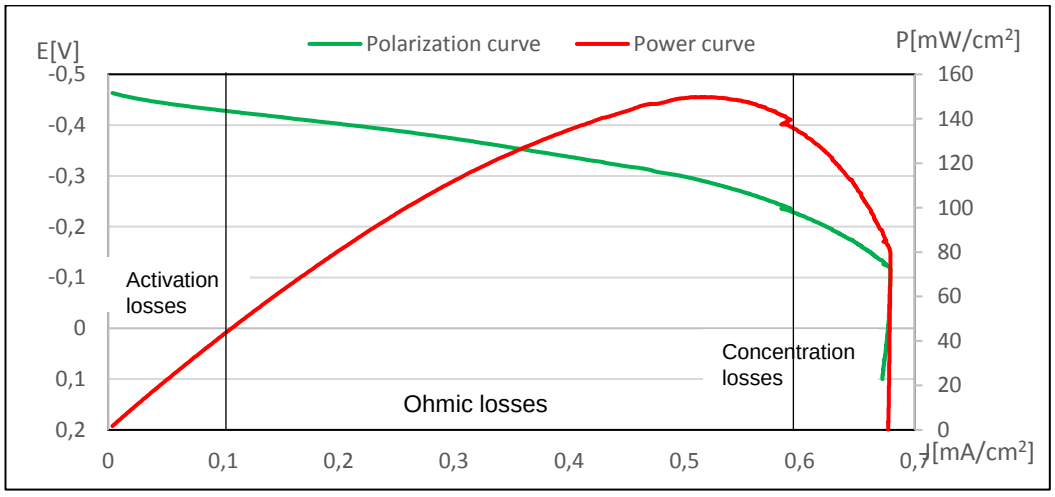

Figure 3. 9 - Polarization and power curves registered for the anode of the MEC1, in the LSV test (courtesy of Eng. Giovannimatteo Erby (IGAG-CNR)

There are two types of analysis that one can do from a CV: *non-turnover* and *turnover*. Because the solution resistivity and cell geometry, in particular the distance between working electrode and reference electrode [54], can be a problem in a *non-turnover* analysis, this one was not performed. The big dimension of the electrode would have led to an interference in the result (the higher the surface area, the bigger overpotential) . So, it was only performed a CV analysis in *turnover* mode and the results, present in the next two graphs were similar to those found in literature [53].

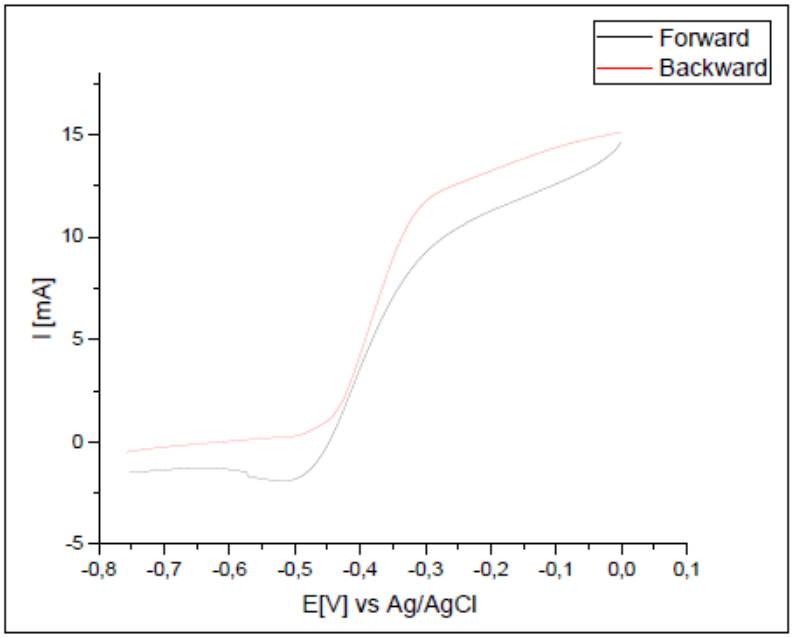

Figure 3. 10 - Cyclic voltammogram from a turnover CV analysis, on the MEC1, (courtesy of Eng. Giovannimatteo Erby (IGAG-CNR)

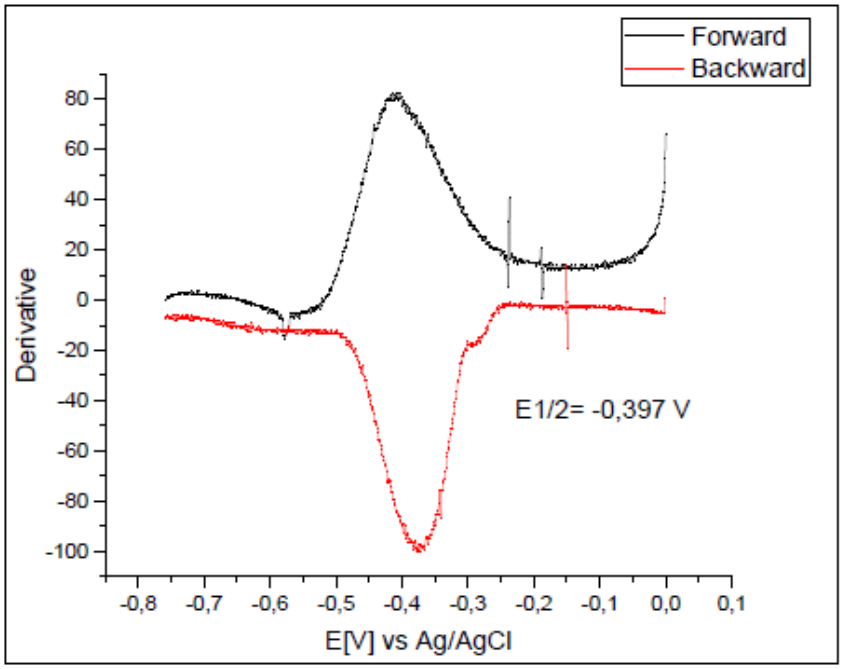

Figure 3. 11 - Derivative chart regarding the applied potential, obtained from the CV turnover curve, of the MEC1 (courtesy of Eng. Giovannimatteo Erby (IGAG-CNR)

The figure 3.11 shows the derivative curve from the first *turnover* graph that allows to determine the half wave potential ($E_{1/2}$), found in the maximum pick of forward curve, and the maximum value for the backward curve. This power value coincides with $E_{1/2}$, meaning that is the value correspondent to the inflexion point of the curve given by the CV analysis. This value is the potential value where the enzymatic reactions progress is at its faster. The $E_{1/2}$ is found to be -0.397 V.

Since the MEC2 had the anode chamber using graphite granules, that may lead to interferences, for this reason no meaningful data was possible to obtain.

3.2.4 Absorption column performance

The ammonia that was stripped from the stripping column was then forced to pass through an adsorption column filled with rashig rings and a solution of 1M of sulfuric acid, leading the recovery of ammonia by ammonium sulphate. The performance of the absorption column maintained about 81% of the mass of ammonia removed in the anolyte. The graph 3.12 indicates that almost every amount of nitrogen that crossed the membrane, into the catholyte, was after absorbed in the absorption column. It is possible to conclude that the MEC system was very efficient in the recovery of the ammonia removed. The graph starts in phase 3 since it was around this time that the absorption column was installed. In phase 5 it is possible to see a significant drop that is consistent with other abnormal values obtained for this period, due to malfunctions. After this malfunction the systems resumed a good performance as it is seen in the end of phase 5 and phase 6.

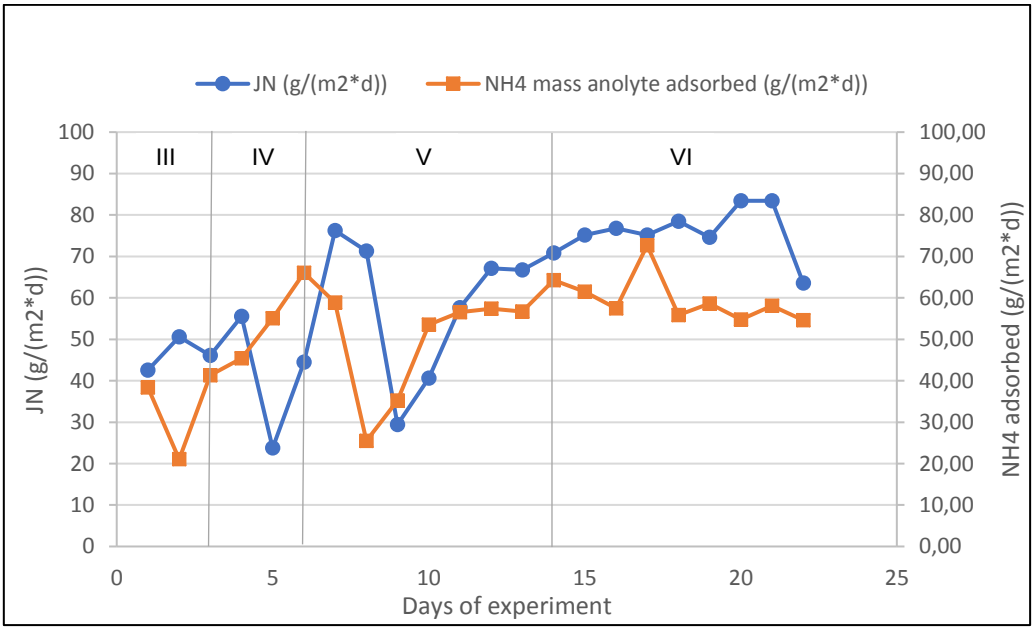

Figure 3. 12 - Progression of the ammonia adsorbed, daily, and the amount of ammonia adsorbed by square meter of the membrane, in MEC1, using SWW

Also, for MEC2 the adsorption values (present in figure 3.13) were constant and about 90% of the ammonia removed from the anolyte. The almost “overlap” of the lines indicates, once again, that almost every amount of nitrogen flowing through the membrane was absorbed after, in the absorption column. The systematic drops in the MEC2 could have been due to malfunctions of the system regarding the flow of nitrogen crossing the membrane due to malfunction of the influent pump. This problem would ultimately compromise the performance of the stripping and absorption columns due to lower quantity of ammonia that was crossing the membrane.

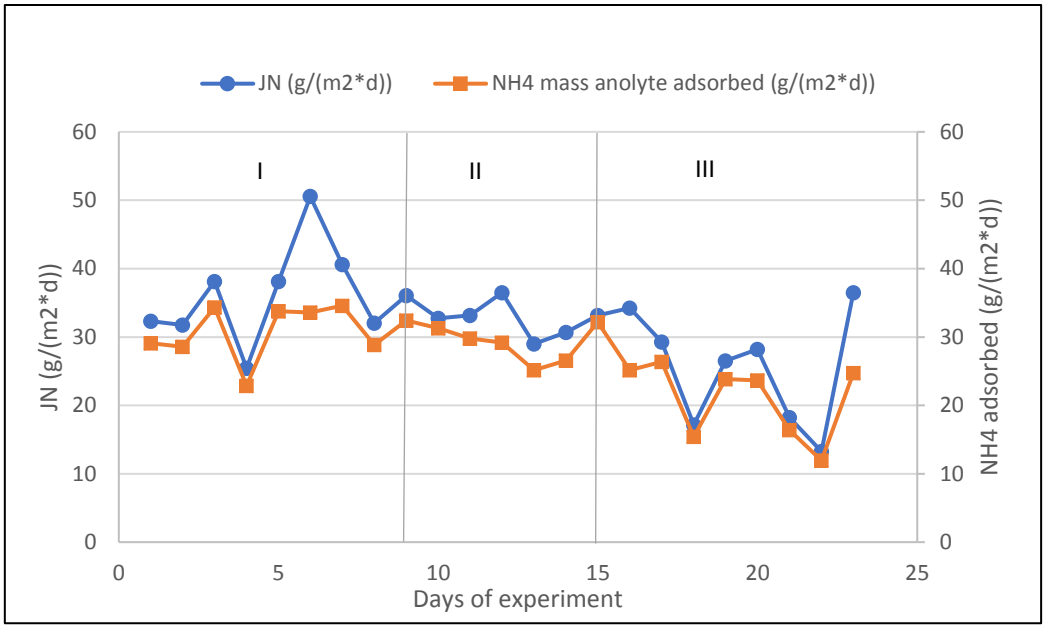

Figure 3. 13 - Progression of the ammonia adsorbed, daily, and the amount of ammonia adsorbed by square meter of the membrane, in MEC2, using SWW

3.3 Real wastewater

This chapter is focused on the performance of MEC1 and MEC2 with real wastewater. MEC1 started using real wastewater after the 18th of May, while MEC2 after de 2nd of May.

3.3.1 Nitrogen recovery

In figure 3.14, we find the progression of the amount of J_N (red line) and that of the removal efficiency, in percentage (blue line), both for the MEC1. The values of both the removal efficiency and grams of ammonia recovered tend to decrease. The use of a wastewater with poor concentration of rapidly biodegradable organic matter can also be a factor that explains this behaviour since it is directly responsible for the lower values of ammonia, and lower conductivity. A low ammonia concentration would reduce even further the performance of the cell over time, also if there was a low concentration in rapidly degradable organic matter wouldn't be possible for the bacteria to perform a good removal and recovery.

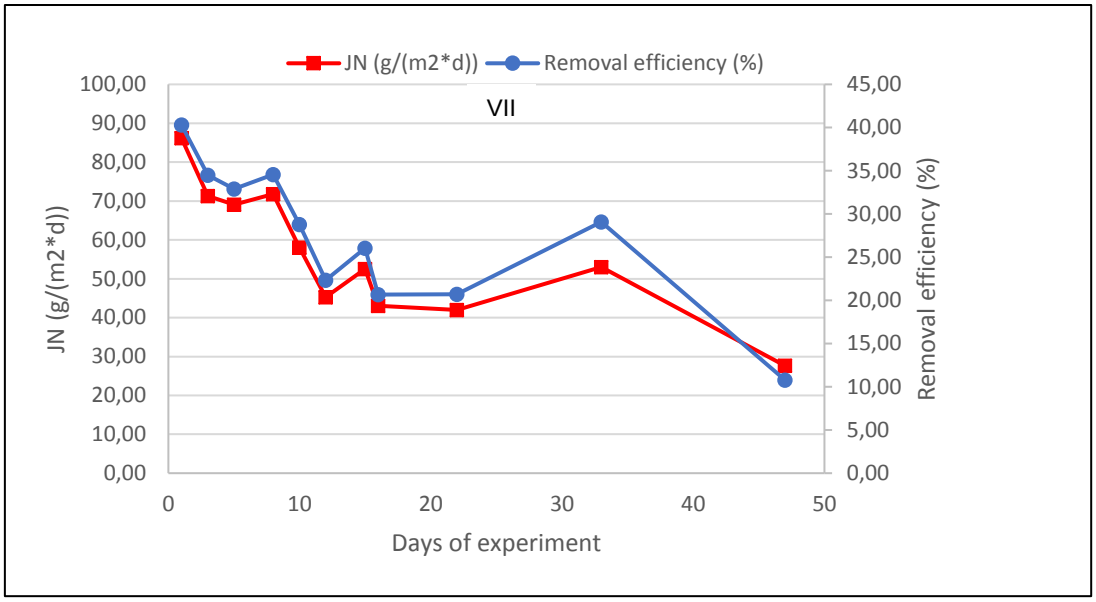

Figure 3. 14 - Removal efficiency and daily nitrogen flux that crosses the membrane, treating real wastewater, for the MEC1

Considering MEC2, removal efficiency was found to be low in the initial phases (around 24%) with an increase in the last phase, coincident with the new stock of the real wastewater. It is possible to observe a significant increase in phase V, in both parameters. The feeding flow that fed the anode chamber was increased in phase V which comes to conclude once again it is directly effect on the values of grams of ammonia recovered, parameter where the change is more obvious. The removal efficiency was also increased but with less effect.

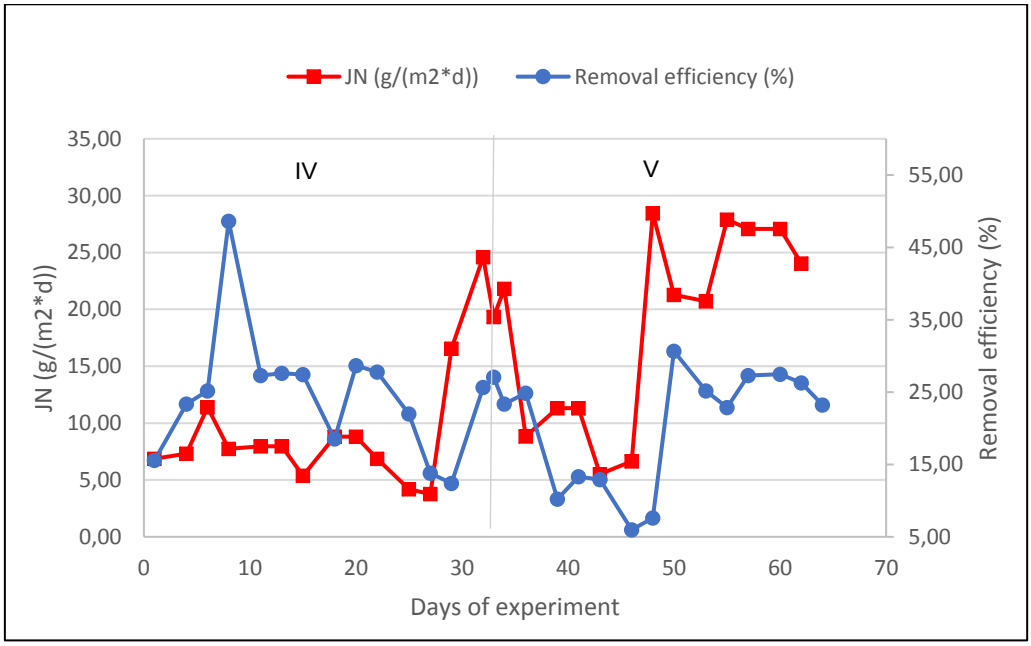

Figure 3. 15 - Removal efficiency and daily nitrogen flux that crosses the membrane, treating real wastewater, for the MEC2

As one can observe, from figure 3.15, the values of both parameters are reducing over phase IV. The reasons are most likely the ones that were presented for the performance of the MEC1,

regarding the removal efficiency and ammonia recovered, in figure 3.14 (new stock of RWW). The increase in phase V lead to a bigger amount of nitrogen crossing the membrane and, of course a larger amount removed. The phase V was characterized by greater ammonia removal efficiency and removal rates, but with high variations during the phase.

Similarly, to the case of the synthetic waste water, also a maximum theoretical value for the nitrogen amount crossing the membrane was calculated and then a ratio was done in order to see how close to this maximum value, the equipment was working. Furthermore, the stripping efficiency was also determined. The parameters obtained can be shown in the following two tables, 3.6 and 3.7.

Table 3. 6 - Parameters regarding the nitrogen recovery, for MEC1, using real wastewater

Day	JN, max g/(m2.d)	JN/JN,max	SE (%)
1	105.40	0.8	35.1
3	103.02	0.7	34.5
5	91.33	0.8	32.9
8	97.02	0.7	34.6
10	69.34	0.8	28.8
12	64.35	0.7	22.3

Table 3. 7 - Parameters regarding the nitrogen recovery, for MEC2, using real wastewater

Day	JN, max g/(m2.d)	JN/JN,max	SE (%)
11	10.42	0.7	27.3
13	13.71	0.6	26.9
15	12.09	0.7	26.0
60	61.84	0.4	24.9
62	34.75	0.8	26.3
64	52.67	0.5	22.6

It can be seen from the former two tables that the MEC1 was working closer to the maximum theoretical value and that it had also higher stripping efficiencies, in percentage. Although the stripping efficiency is higher in MEC1, one can see that the values are never higher than 36% which means low stripping efficiency. This can be due to the fact that the slow organic matter degradation (and electron production) and consequently J_N decrease, led to a small amount of ammonium crossing the membrane, which ultimately meant a low amount of ammonia stripped.

The MEC1 cell showed a 56.36 g/m^2 value of nitrogen crossing the membrane, on a daily basis, showing a promising future for the MEC technology even with real wastewater. With the absorption column working with an efficacy of 90 to 95%, most of this nitrogen was able to be recovered.

MEC2 did not show a performance as good as MEC1, showing 13.80 g/m^2 of nitrogen recovered daily. The column also worked with similar efficacy as the MEC1 did (90-95%). However, this value shows that there is still room for improvement in order to obtain better performances. This also shows that carbon felt in the MEC1 leads to a better performance in the recovery of the nitrogen instead of the graphite granules, present in the MEC2 anode chamber.

The next table (3.8) as one can find for the synthetic wastewater analysis, it can be found the values of the nitrogen concentration in the influent, by phase. Since the true value of the concentration of ammonia wasn't possible to obtain, an average value was made from all the concentration of the influent measured throughout the experiment.

Table 3. 8 - Removal efficiency and nitrogen flow through the membrane, for both cells, for every phase

MEC1					MEC2				
Phase	N-NH4 influent conc. (mg/L)	HRT (h)	RE (%)	JN (g/(d*m2))	Phase	N-NH4 influent conc. (mg/L)	HRT (h)	RE (%)	JN (g/(d*m2))
VII	2800	6	27.3±8.3	56.4±16.9	IV	1009	8	24.6±8.9	7.7±3.3
					V	2271	8	20.6±7.9	19.1±7.9

The MEC1 showed the highest stripping efficiency and higher removal efficiency, in comparison with MEC2. Since no additional change was made to the raw state of the equipment, the conclusion that can be taken from this analysis to real wastewater is that the carbon felt in MEC1 was directly responsible for a better performance, in comparison to the graphite granules of the MEC2.

3.3.2 Alkalinity

The alkalinity in the waters is mostly a function of carbonates, bicarbonates and hydroxides content in the samples [56]. In this case, the alkalinity test was performed measuring the amount of calcium bicarbonate, in each sample.

In the following graph, there will be found values of the amount of calcium bicarbonate g/L in each sample (influent and effluent).

Here we have an example of a bad performance of the cell since we did not have an evident decrease in alkalinity, as one would expect. It can also be seen that the difference between alkalinity values of influent and effluent have come to decrease more and more over days, which can also mean that the cell had started earlier to work in a worse way. In the first days we have a normal consumption of alkalinity, as it was expected.

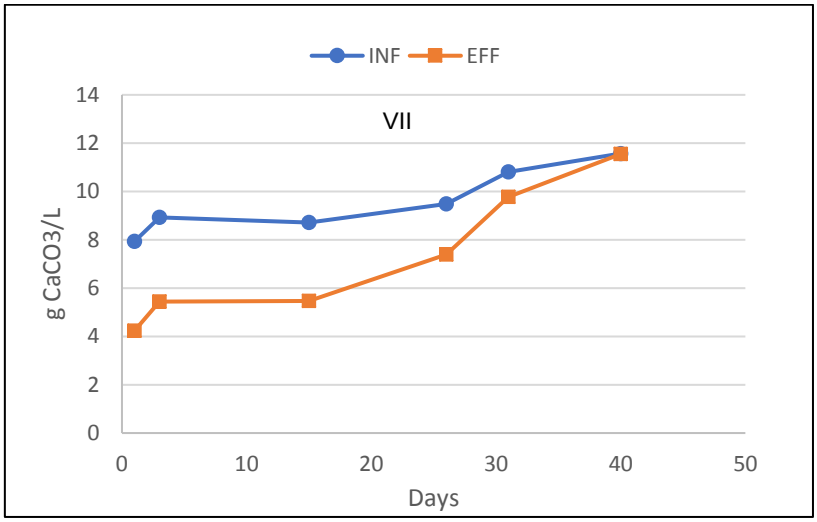

Figure 3. 16 - g CaCO3/L, for MEC1, using real wastewater

In the following graph (3.17) we find the same test, for the MEC2. In this scenario is more obvious the low differences between the alkalinity measured in the influent and in the effluent. MEC2 was the first cell using real wastewaters and for a time it was working with old wastewaters. Since it is not possible to verify the amount of protons, ammonia concentration and other parameters already described before, it is hard to predict what led to these observations. However, the data is consistent with the low performance of the MEC2 regarding removal efficiency and nitrogen crossing the membrane.

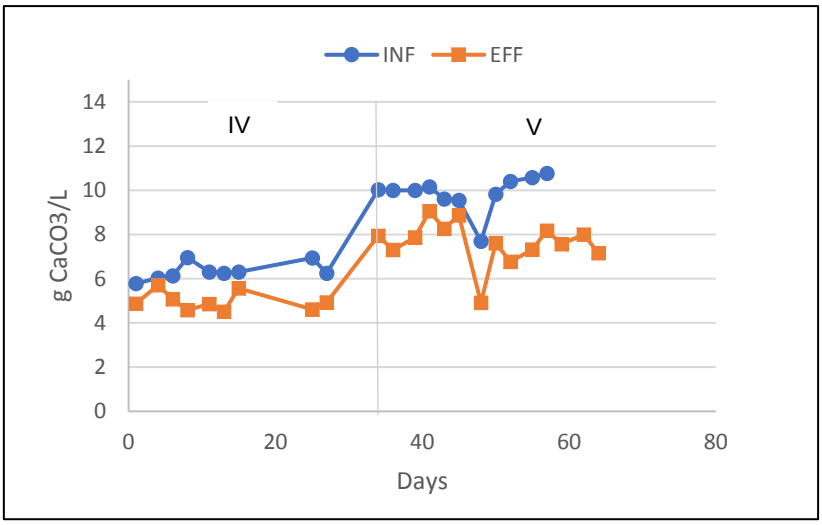

Figure 3. 17 - g $CaCO_3$/L, for MEC2, using real wastewater

3.3.3 COD

Chemical oxygen demand is an important quality analysis for a wastewater that allow to quantify the equivalents of oxygen necessary to oxidize the organic and inorganic substance present in a sample.

It is imperative for a waste water treatment plant or process in order to know how much of a specific oxidant is present in the water, that may react with the sample, under controlled conditions [57]. It is important that the amount of this oxidant isn't too big because it will lead to a large consumption by the microorganisms. The higher the amount of COD, the higher the amount of pollutant content. The quantity of COD consumed is expressed as its oxygen equivalence, hence is defined as mass of O_2 (in this case mg) per liter.

In table 3.9 we have the results for the COD test, on MEC1 filtered samples.

Table 3. 9 - COD test results, for MEC1, using real wastewater

Date	Sample	COD (mg O_2/L)	RE%
22/06/2018	MEC1 EFF	3500	32.7%
27/06/2018	MEC1 EFF	4800	7.7%
06/07/2018	MEC1 EFF	5100	1.9%

The high amounts of COD and low removal efficiencies indicate that there is still a great amount of oxidizable substrate in which bacteria could feed on. These values are also an indication that the system still needs improvements in order to lower the COD. High values for COD also means

that if the wastewater was to return to the nature, after “treatment” it would be a pollutant since there would still be a great amount of oxidizable matter that would be consumed by bacteria that in the process would consume the dissolved oxygen in the water leading to possible eutrophication.

In the following table, 3.10, we have the same study regarding MEC2.

Table 3. 10 - COD test results, for MEC2. using real wastewater

Date	Sample	COD (mg O_2/L)	RE%
05/06/2018	MEC2 EFF	3200	25.6%
06/06/2018	MEC2 EFF	3500	18.6%
13/06/2018	MEC2 EFF	2700	37.2%
15/06/2018	MEC2 EFF	4000	7.0%
20/06/2018	MEC2 EFF	3300	23.3%
22/06/2018	MEC2 INF	4300	-
22/06/2018	MEC2 EFF	3600	16.3%

MEC2 had a better overall performance than MEC1 but as it is seen by table 3.10, the COD removal efficiencies are still quite low, showing that there is still a lot of oxidizable matter in the wastewater, even after treatment. Also MEC2 needs improvements regarding COD reduction.

3.3.4 Electric performance

Like in the case of synthetic wastewater, a chronoamperometric test was done. The values of the produced current density are shown in figure 3.18. As it is shown, there is an evident group of values of current density that are extremely low, almost inexistent.

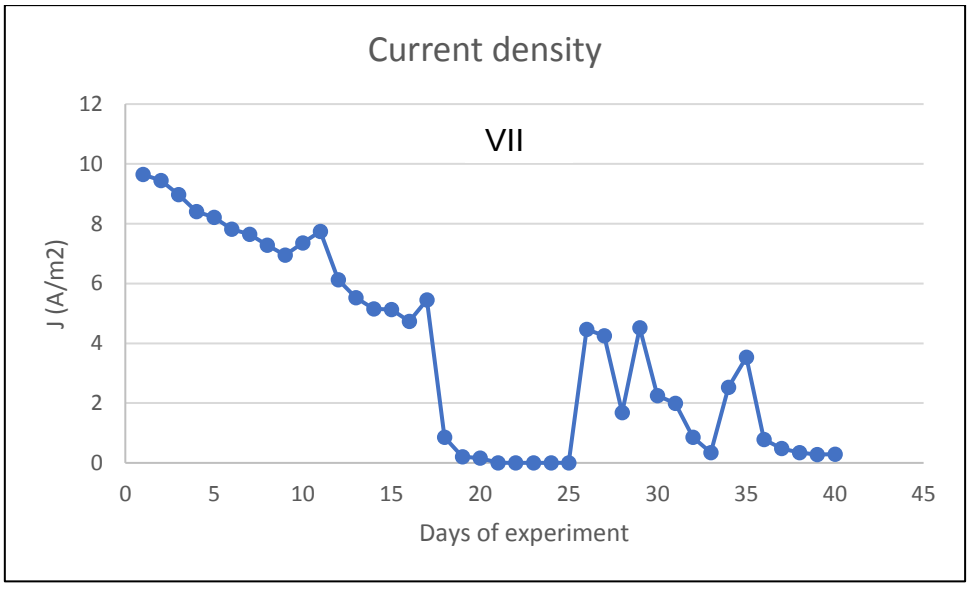

Figure 3. 18 - Current density progression, for MEC1, using realwastewater

Figure 3.19 shows consistent results, for the same days where the current density values were extremely low showing that there was some kind of malfunction with the MEC1, during this period.

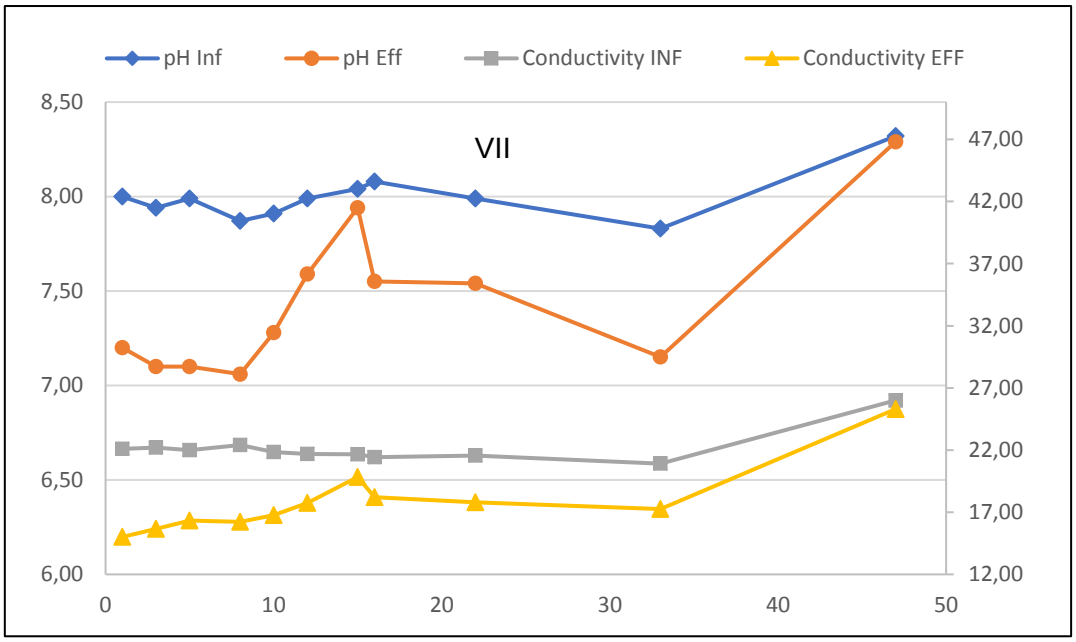

Figure 3. 19 - pH and conductivity, for MEC1, using real wastewater

In figure 3.20, the same profile of current density is shown for MEC2. The figure shows a growing behaviour that starts with very low results in the beginning but then sudden increase. A similar result is shown in figure 3.21, where conductivity values for this same period show a similar behaviour. A larger number of ions would lead to greater values of conductivity but lower ones for pH. This same thought takes place in the beginning of the experiment since the pH shows higher values showing a low number of ions in the anolyte influent and effluent, which would ultimately lead to lower values for conductivity and for current density. Once again, pH and conductivity values show important information regarding current density behaviour and the overall performance of the cells.

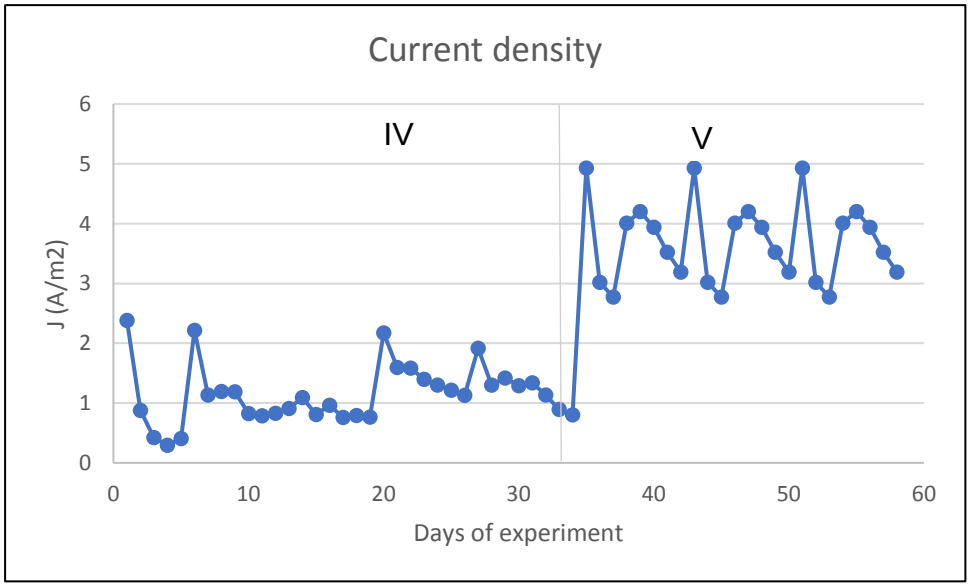

Figure 3. 20 - Current density progression, for the MEC 2, using real wastewater

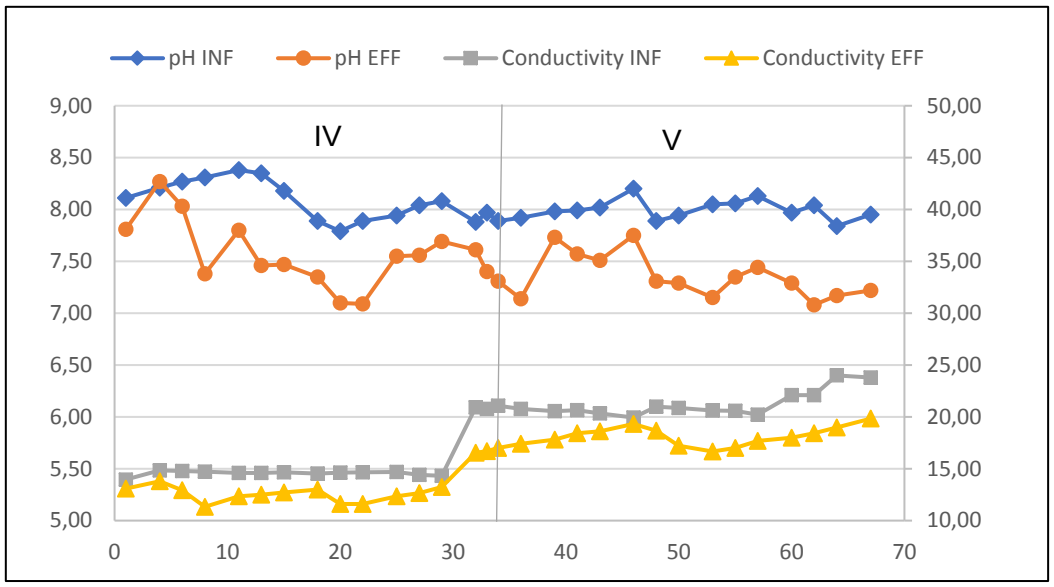

Figure 3. 21 - pH and conductivity, for MEC2, using real wastewater

The chronoamperometry test done for the real wastewater helped to obtain values of current density that were after used in determining current density, coulombic efficiency and energy to give to the cell to help extract the ammonia, the same as it was done for the MEC1. The formulas used were the same as the ones used for MEC1. In the following two tables we find these same control parameters values.

Table 3. 11 - Values of the current density, coulombic efficiency and energy, for MEC1, using real wastewater

Phase	J (A/m2)	CE (%)	EN (kWhkg/N)
VII	8.3±1.0	69.6±7.9	3.6±0.3

Table 3. 12 - Values of the current density, coulombic efficiency and energy for MEC2, using real wastewater

Phase	J (A/m2)	CE (%)	EN (kWhkg/N)
IV	1.4±0.7	46.5±24.4	6.0±4.3
V	3.1±1.3	36.4±24.4	3.7±1.1

During the time of the experiment using real wastewater MEC1 showed a current density of 8.3 $A.m^{-2.}$ a coulombic efficiency of 69.6% and 3.6 $kWhkg.N^{-1}$ whereas MEC2 had 3.1 $A.m^{-2}$, 46.5% and 6 $kWhkg.N^{-1}$, for the same parameters. The MEC1 showed to be more self sustained.

3.3.5 Absorption column performance

The next two graphs (3.22 and 3.23) are also in a similar scenario as the others for SWW. It is almost shown an overlap between the nitrogen removed and the one absorbed. The column didn't show failure or malfunctions, keeping the removal rates of 90% (on average) for MEC1 and 37% for MEC2. This indicates that the change for real wastewater did not necessarily had a secondary worse performance as consequence, showing a good nitrogen recovery performance. MEC2 had a worse performance not because of the change but most likely due to technical malfunction of the system (gas leakage in the tubes from the stripping column to the absorption column).

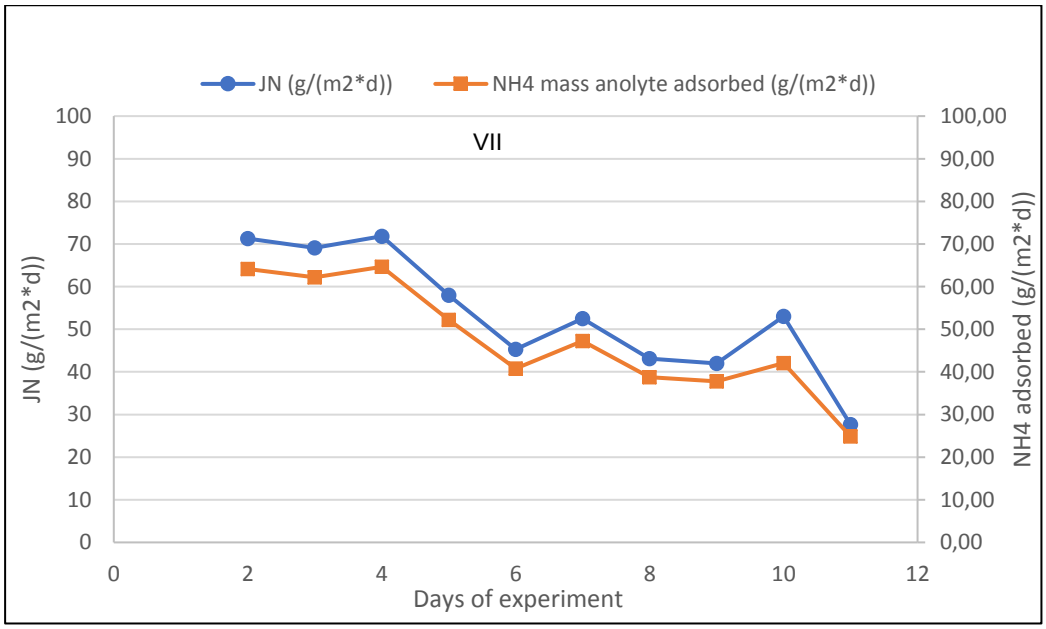

Figure 3. 22 - Progression of the ammonia adsorbed, daily, and the amount of ammonia adsorbed by square meter of the membrane, in MEC1, using RWW

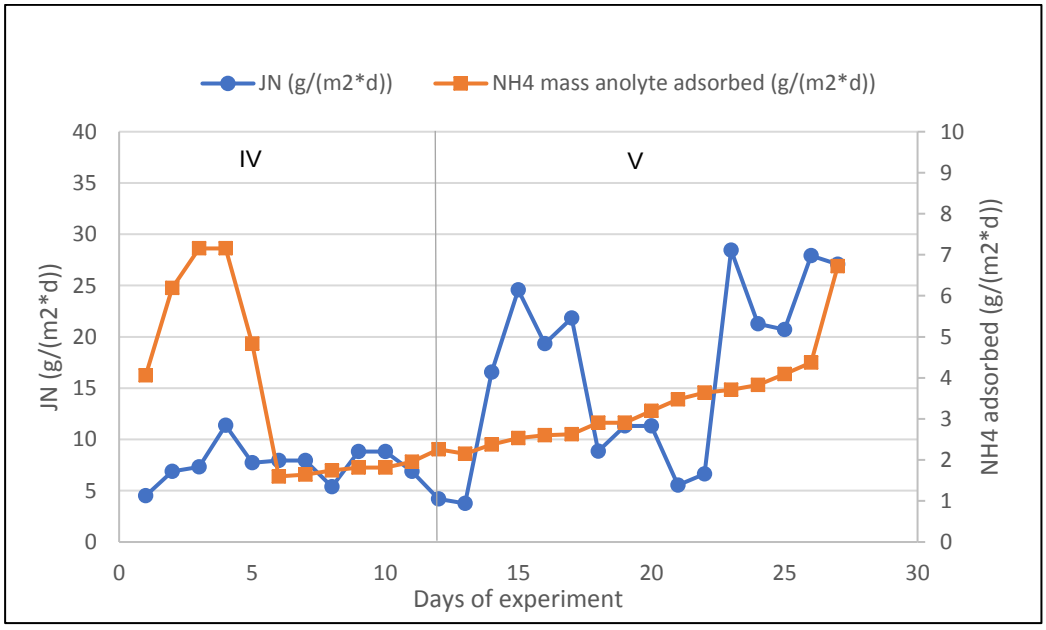

Figure 3. 23 - Progression of the ammonia adsorbed, daily, and the amount of ammonia adsorbed by square meter of the membrane, in MEC2, using RWW

4

Conclusions and future work

The increase growth of the world population has been leading to an increase demand of food supply. Most crops rely on fertilizers that are nitrogen (in the form of ammonia) based. The ammonia cannot be all used so a good amount ends up in the lower water bodies and soils. This contamination leads to uncontrolled growth of algae and bacteria in a phenomenon called eutrophication. The recovery of this nutrient can lead to environment sustaintability and economical profit by making the use of this cyclic nutrient. BES systems can oxidize substrates enriched with ammonia, with the aid of anaerobic bacteria. In this oxidation, electrons and protons are released as well as nitrogen, in its ammoniu form, that can after be removed and collected in an absorption column, as ammonia. This experiment was conducted with an MEC type of BES. The experiment was driven in two big phases: using synthetic wastewater and using real wastewater. It had been proven that MEC technology could efficiently remove ammonia and achieve high coulombic efficiencies as well as current densities.

In an overall performance outlook, it can be seen that the use of carbon felt (in the MEC1) leads to better removal efficiencies and higher removal rates than the ones when using graphite granules (presented in MEC2). Being the anode material the only big difference between the 2 systems, it is possible to conclude that our system has a better performance using carbon felt than graphite granules. When experiencing with real wastewaters, it was possible to see that the overall performance of the MECs was worse than the performance when using synthetic wastewater. MEC1 had a removal efficiency of 27.3% and a removal rate of 56.4 g $N\text{-}NH_4^+/(m^2*d)$ and MEC2 24.6% and 19.1 g $N\text{-}NH_4^+/(m^2*d)$ for the same parameters, respectively. The characteristics of the real wastewater treated, with more complex organic substance than only acetate could be highly related to the worse performance of the system. Moreover, the variability of the real wastewater provided during time is highly linked to the variations of the performance for both MECs.

When using synthetic wastewater, MEC1 had a current density production of 9 A/m^2 and a 66.7% coulombic efficiency, whereas MEC2 had 5.1 A/m^2 and 61.8%, for the same parameters. These results did not differ highly from the ones conducted with real wastewater (8.3 A/m^2 and 69.6% for MEC1 and 3.1 A/m^2 with 46.5% for the MEC2). There was a significant drop in the coulombic efficiency of the MEC2 when using real wastewater, but the overall performance was promising and not far off from the results obtained from literature.

The use of MEC technology with real wastewater showed to be promising regarding ammonia removal but further studies are in order, especially in the topic of scale up. The system losses become higher when the dimension of electrodes, membrane, reactors, etc, are increased [58].

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