

Article

Biogas Upgrading and Ammonia Recovery from Livestock Manure Digestates in a Combined Electromethanogenic Biocathode—Hydrophobic Membrane System

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Abstract: Anaerobic digestion process can be improved in combination with bioelectrochemical systems in order to recover energy and resources from digestates. An electromethanogenic microbial electrolysis cell (MEC) coupled to an ammonia recovery system based on hydrophobic membranes (ARS-HM) has been developed in order to recover ammonia, reduce organic matter content and upgrade biogas from digested pig slurry. A lab-scale dual-chamber MEC was equipped with a cation exchange membrane (CEM) and ARS with a hydrophobic membrane in the catholyte recirculation loop, to promote ammonia migration and absorption in an acidic solution. On the other hand, an electromethanogenic biofilm was developed in the biocathode to promote the transformation of CO₂ into methane. The average nitrogen transference through the CEM was of 0.36 g_N m⁻² h⁻¹ with a removal efficiency of 31%, with the ARS-HM in the catholyte recirculation loop. The removal of ammonia from the cathode compartment helped to maintain a lower pH value for the electromethanogenic biomass (7.69 with the ARS-HM, against 8.88 without ARS-HM) and boosted methane production from 50 L m⁻³ d⁻¹ to 73 L m⁻³ d⁻¹. Results have shown that the integration of an electromethanogenic MEC with an ARS-HM allows for the concomitant recovery of energy and ammonia from high strength wastewater digestates.

Keywords: microbial electrolysis cell; biocathode; electromethanogenesis; ammonia recovery; hydrophobic membrane



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1. Introduction

The combination of the well-established anaerobic digestion technology with bioelectrochemical systems (BES) has been subject of wide study in the last decade, since multiple configurations and objectives have been addressed [1–3]. BES can help to overcome many of the drawbacks of anaerobic digestion, such as process instability [1,4,5], polishing of effluents and recovery of nutrients from the digestate [6–10], or biogas upgrading [11–15].

Anaerobic digestion of high organic and nitrogen strength wastewater, such as livestock manure, provides the possibility of being combined with BES in order to simultaneously recover ammonia from the digestate and to enhance energy recovery from the substrate, by converting the CO₂ contained in the biogas into CH₄ [11].

In the new framework of circular economy, ammonia recovery from waste streams is a sustainable alternative preferred to the industrial production by nitrogen fixation (Haber-Bosch process). BES have been proved to be a suitable technology for ammonia recovery, using dual chamber cells and cationic exchange membranes (CEM), either in the form of energy producing microbial fuel cells (MFC) or by introducing a small amount of energy to boost the process using microbial electrolysis cells (MEC) [16]. Ammonium, present in the substrate fed into the anode compartment of the cell, migrates through the CEM towards the cathode compartment, concomitant to the electron movement from the

anode to the cathode through the external circuit, in order to maintain the electroneutrality of the reactor [17,18].

On the other hand, electromethanogenesis in MEC is based on the conversion of CO_2 into CH_4 , which is an advantage over other biogas upgrading technologies, based on the separation of CO_2 from the biogas stream. The development of a biofilm on the cathode of a MEC, fed with CO_2 , and the application of the suitable potential (usually between -0.6 V and -1 V), leads to the production of CH_4 . Electromethanogenesis has been reported to take place by two electron transfer routes: (i) direct and (ii) indirect electron transfer. In the direct electron transfer route, CO_2 is combined by exoelectrogenic bacteria with protons and electrons, accepted directly from the cathode, to produce CH_4 . In the indirect route, protons are previously transformed into H_2 , which in turn is used by electroactive microbes to reduce CO_2 (hydrogenotrophic methanogenesis). Electromethanogenic MECs have been the subject of recent reviews [19,20], including the combination with anaerobic digestion set-up [13,21].

Previous works have demonstrated the feasibility of an electromethanogenic biocathode MEC to produce methane from CO_2 and to remove ammonium from digestates, but a final step for ammonia recovery from the catholyte should be further addressed [11]. Stripping/absorption processes have been tested in an abiotic cathode MEC as a system to recover ammonia from the catholyte, enhanced by the increase in pH (with values in the range of 9–12) produced in the cathode compartment [4,6]. The main drawback to complete the recovery process in a biocathode, compared to an abiotic cathode MEC, is that pH in the catholyte needs to be controlled in a range suitable for microorganisms' development [22]. This neutral pH requirement makes ammonia stripping less favorable and energy demanding if forced by high temperature [23]. Furthermore, biomass from the biocathode could move with the gas flow and accumulate in the absorbent of the stripping system [24].

An alternative to ammonia stripping for electromethanogenic biocathodes could be hydrophobic membranes, which are permeable to gases. Ammonia gas dissolved in a liquid stream can traverse the pores of the hydrophobic membrane and react with an acidic solution placed on the other side [25,26]. The use of these membranes coupled to the ammonium migration in a MEC could allow for the recovery of ammonia at close to neutral pH and reduce the energy demand of the recovery step compared to the stripping/absorption process. Gas-permeable hydrophobic membranes have been successfully employed in MECs as a proton shuttle to improve the MEC performance [27], or for ammonia recovery from urine [9,28]. Liquid-liquid membrane contactors have been tested in ammonia recovery with different acids as absorbents for fertilizer production [29].

This work assesses for the first time the use of hydrophobic membranes to recover ammonia from high organic and nitrogen strength digestates in a MEC, while upgrading biogas in an electromethanogenic biocathode, working at near to neutrality pH.

The aim of this study is to evaluate an electromethanogenic microbial electrolysis cell (MEC) coupled to an ammonia recovery system based on hydrophobic membranes (ARS-HM) in order to recover ammonia, reduce organic matter content and upgrade biogas from digested pig slurry. This assessment is going to be performed in a continuously fed operation mode reactor. The feasibility of recovering ammonia from the biocathode compartment using the ARS-HM while maintaining an optimum pH for biomass will be addressed by measuring nitrogen flux through the membranes. Methane production will be monitored in order to assess if biocathode performance is improved by the ARS-HM connection.

2. Materials and Methods

2.1. Experimental Set-Up

A two-chamber cell (0.5 L each compartment) was constructed using methacrylate, following the design described elsewhere [7]. A cation exchange membrane (CEM, dimensions: 168 cm^2 ; Ultrex CMI-7000, Membranes International Inc., Ringwood, NJ, USA) was placed

between anode and cathode compartments. A piece of carbon felt (dimensions: 168 cm²; thickness: 3.18 mm; Alfa Aesar GmbH and Co. KG, Karlsruhe, Germany) was used as anode, while granular graphite was used as cathode, with diameter ranging from 1 mm to 5 mm (Typ 00514, enViro-cell Umwelttechnik GmbH, Oberursel, Germany). A 304 stainless steel mesh was used as electron collector in both chambers (dimensions: 168 cm²; mesh width: 150 μm; wire thickness: 112 μm; Feval Filtros, Barcelona, Spain).

An ammonia recovery system based on hydrophobic membranes (ARS-HM) was integrated in the recirculation loop of the catholyte (Figure 1). Two glass bottles (0.25 L each one) with a side opening were connected, inserting a polytetrafluorethylene (PTFE) membrane (0.45 μm pore size, Filter-Lab, Filtros Anioia, S.A., Sant Pere de Riudebitlles, Spain), achieving a free area of 10 cm². One of the chambers was fed in continuous mode with catholyte, while the second chamber, the ammonia recovery chamber (ARC), was filled with an acidic solution (H₂SO₄, 1.8 M) and operated in batch mode. Both chambers were equipped with a magnetic stirrer.

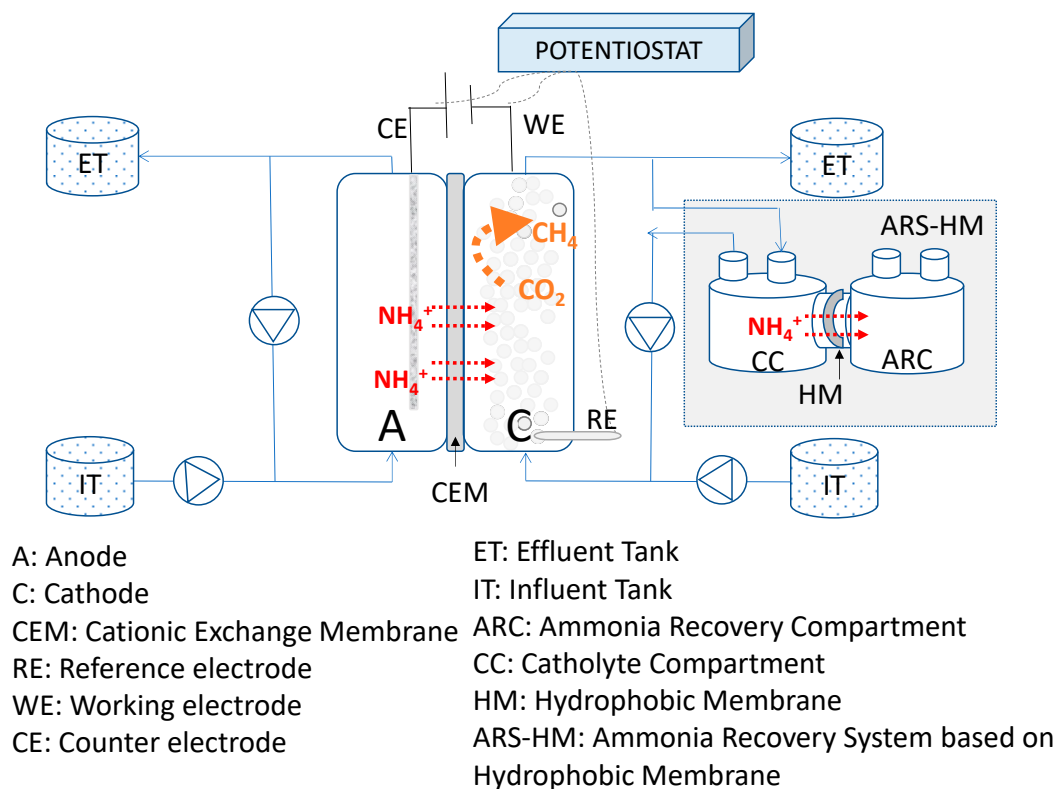


Figure 1. Schematic diagram of the set-up of the dual-chamber microbial electrolysis cells (MEC) with an electromethanogenic cathode and the ammonia recovery system based on hydrophobic membranes (ARS-HM) connected in the catholyte recirculation loop.

The cathode (working electrode) was poised at a potential of -800 mV, in a three-electrode mode, by a potentiostat (VSP, Bio-Logic, Grenoble, France). An Ag/AgCl reference electrode (Bioanalytical Systems, Inc., West Lafayette, IN, USA; $+197$ mV vs. standard hydrogen electrode, SHE) was inserted in the cathode compartment. All potential values in this paper are referred to SHE. The potentiostat was connected to a personal computer, which recorded electrode potentials and current, every 5 min, using EC-Lab software (Bio-Logic, Grenoble, France).

2.2. Feeding Solutions

The digestate used to feed the anode compartment of the MEC was collected from a lab-scale thermophilic anaerobic digester, which was fed with pig slurry. The digestate was

stored at 6 °C until its use and sieved (125 µm) and was characterized as follows: pH of 8.2 ± 0.2 , COD of $16.5 \pm 3.9 \text{ g}_{\text{O}_2} \text{ L}^{-1}$ and $\text{NH}_4^+\text{-N}$ of $1.5 \pm 0.3 \text{ g L}^{-1}$.

The cathode compartment was fed with a synthetic solution containing a source of CO_2 , composed by (per litre of deionized water): NaHCO_3 , 5 g; NH_4Cl , 0.87 g; CaCl_2 , 14.7 mg; KH_2PO_4 , 3 g; Na_2HPO_4 , 6 g; MgSO_4 , 0.246 g; and 1 mL L^{-1} of a trace elements solution [30].

2.3. Reactor Operation

The bioanode of the MEC was operated with digested pig slurry, inoculated previously with the anode compartment effluent from a lab-scale MEC operated with synthetic solution. The cathode compartment was inoculated with graphite granules from a previously operated electromethanogenic biocathode [11].

The influent solutions of both the anode and the cathode compartments were fed in continuous mode with a pump at 20 mL h^{-1} and mixed by recirculating them by an external pump. The hydraulic retention time (HRT) of each compartment was of 35 h, 17 h and 18 h for the anode, cathode and ARS-HM catholyte compartment, respectively (with respect to the net volume of each compartment), and the organic loading rate (OLR) of the anode compartment was established at $12 \text{ kg}_{\text{COD}} \text{ m}^{-3} \text{ day}^{-1}$. Samples of the anode and cathode compartment effluents and from the ARC were taken three times per week. The MEC was operated at room temperature during the entire assay ($23 \pm 2 \text{ }^\circ\text{C}$).

2.4. Organisation of Experiments

After a start-up period, the MEC was operated for 40 days. On day 24, the ARS-HM was connected in the catholyte recirculation loop in order to study the effect of ammonia recovery on the MEC performance (Table 1).

Table 1. Different phases and operation conditions of the MEC.

Phase	Period (d)	ARS-HM Connection
1	1–24	No
2	25–40	Yes

2.5. Analytical Methods and Calculations

Chemical oxygen demand (COD) was determined in anolyte feeding and anode compartment effluent samples. Ammonium nitrogen ($\text{NH}_4^+\text{-N}$) and pH were determined in the anolyte and catholyte effluent and acidic solution samples. All the analyses were performed following standard methods [31]. The bulk solution pH in each sample was measured using a CRISON 2000 pH electrode (Hach Lanhe Spain, S.L.U., L'Hospitalet de Llobregat, Spain). $\text{NH}_4^+\text{-N}$ was analyzed by a Büchi Kjelflex K-360 distiller (Büchi Labortechnik AG, Flawil, Switzerland) and a Metrohm 702 SM autotitrator (Metrohm AG, Herisau, Switzerland).

Methane was measured in the cathode samples according to Henry's Law and the following method [32], through the determination of dissolved methane. Around 2 mL catholyte samples were collected with a 5 mL syringe and injected with a needle in a 4 mL vacutainer. The vacutainers were shaken vigorously for 30 s and then allowed to stand for 1 h. Headspace gas was analyzed for CH_4 using a VARIAN CP-3800 (Varian Medical Systems, Inc., Palo Alto, CA, USA) gas chromatograph equipped with a thermal conductivity detector (TCD). Dissolved CH_4 was computed using the equation:

$$X_L = \frac{C_{\text{CH}_4} \cdot MV_{\text{CH}_4} \cdot MW_{\text{CH}_4} \cdot (V_T - V_L + \alpha V_L) \cdot 1000}{V_L} \quad (1)$$

where X_L is the concentration of CH_4 (mg L^{-1}) in the solution, C_{CH_4} is the concentration of CH_4 (%) in the headspace 1 h after shaking, MV_{CH_4} is the molar volume of CH_4 at $25 \text{ }^\circ\text{C}$

(0.041 mol L^{-1}), MW_{CH_4} is the molecular weight of CH_4 (16 g mol^{-1}), V_T is the volume (mL) of the vacutainer, V_L is the volume (mL) of the solution and α is the water:air partition coefficient at $25 \text{ }^\circ\text{C}$ (0.03). Methane production was normalized to the net volume of the cathode compartment (0.265 L).

The current density (A m^{-3}) of the MEC was calculated as the quotient between the intensity recorded by the potentiostat (A) and the net volume of the cathode compartment (m^3). COD and ammonium removal efficiencies from the anode compartment were calculated as the ratio of the difference between the anode compartment influent and effluent concentrations and the influent concentration. Ammonia flux through the membranes ($\text{g N m}^{-2} \text{ h}^{-1}$) was calculated as the ratio between the amount of ammonium transferred (g) and the elapsed time (h) and the membrane surface (m^2).

The cathodic CH_4 recovery per unit current consumed (r_{cat}) was calculated according to the following equation [33]:

$$r_{\text{cat}} = \frac{n_m \cdot b \cdot F}{\int_0^t I dt} \quad (2)$$

where n_m is the number of moles of CH_4 produced, I is the current intensity of the period t , b is the number of electrons consumed per mole of CH_4 produced ($8 \text{ mol}_{\text{e}^-} \text{ mol}_{\text{CH}_4}^{-1}$) and F is Faraday's constant ($96485 \text{ C mol}_{\text{e}^-}^{-1}$).

Energy consumption for CH_4 production from CO_2 (kWh m^{-3}) was calculated as:

$$E = \frac{V \cdot I \cdot t}{F_{\text{CH}_4}} \quad (3)$$

where V is the applied voltage (V) and F_{CH_4} is the flow rate of methane produced in the cathode compartment ($\text{m}^3 \text{ d}^{-1}$).

A balance of charge was performed to evaluate the number of electrons that were used for ammonium migration and methane production. When calculating charge, Q , a distinction was made between transport of negative charges in the form of electrons through the electric circuit, Q^- , and transport of positive charges in the form of NH_4^+ through the membrane, Q^+ . Total charge production, Q^- , expressed in coulombs (C) was determined by integrating current over time. Transport of positive charges in the form of ammonium in the system through the membrane, Q^+ , expressed in coulombs (C) was determined as follows:

$$Q^+ = (x_i - x_e) \cdot f \cdot t \cdot z \cdot F \quad (4)$$

with x_i and x_e the molar concentration of ammonium of the anode compartment influent and effluent, respectively, expressed in mol L^{-1} (M), f the feeding flow expressed in L day^{-1} , z the valence of ammonium (1) and F the Faraday constant defined before.

2.6. Statistical Analysis

Data were analyzed using one-way analysis of variance (ANOVA). Whenever significant differences of means were found, the Tukey test at the 5% significance level was performed for separation of means. Statistical analysis was performed using the R software package (R project for statistical computing, <http://www.r-project.org>). Linear adjustments were obtained with a linear regression model in MS Excel.

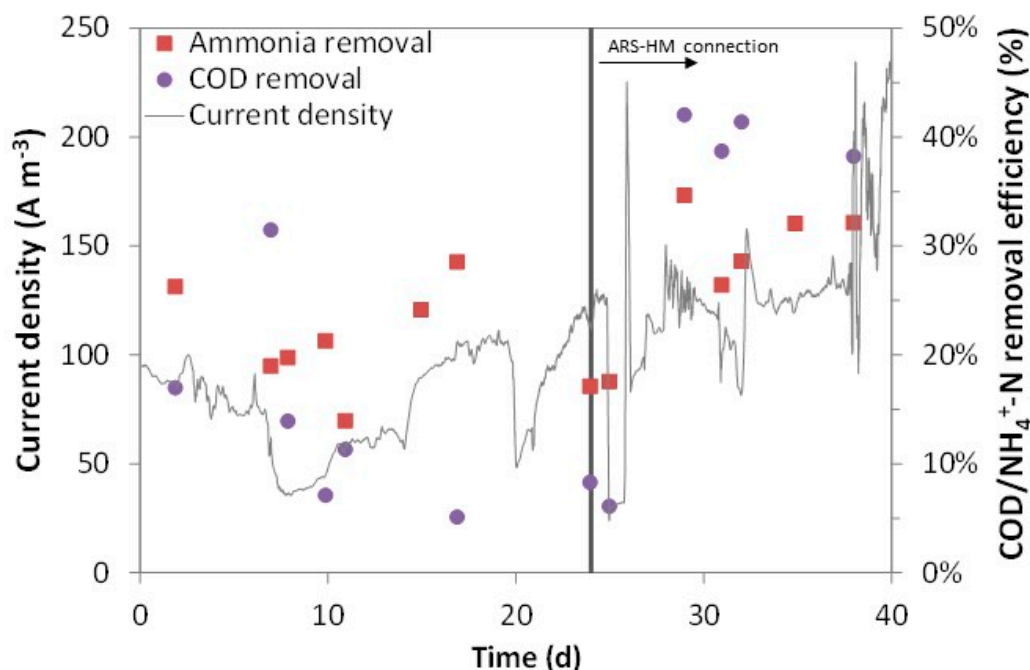
3. Results and Discussion

3.1. General Performance of the MEC and Electromethanogenic Biocathode

After the start-up period (data not shown), the MEC was operated for 24 days with the ARS-HM disconnected, achieving an average current density of $79 \pm 23 \text{ A m}^{-3}$ (Table 2). When the ARS-HM was introduced in the catholyte recirculation loop, on day 25, the current density showed a slight increase in the following days (Figure 2), not statistically significant, up to an average value of $121 \pm 48 \text{ A m}^{-3}$ (Table 2). This increase in current density was concomitant to an improvement in COD removal efficiency, increasing to 40% (15% in the previous phase, $p < 0.05$).

Table 2. Average values for the main performance parameters of the MEC related to methane production.

Phase	Current Density ($A m^{-3}$)	COD Removal Efficiency (%)	Methane Production ($L_{CH_4} m^{-3} d^{-1}$)	Cathodic CH_4 Recovery, r_{cat} (%)
1	79 ± 23	15 ± 9	50 ± 17	27 ± 3
2	121 ± 48	40 ± 2	73 ± 8	23 ± 3

**Figure 2.** Current density production of the MEC and chemical oxygen demand (COD) and ammonium nitrogen (NH_4^+-N) removal efficiencies, in the periods of MEC operation with disconnected and connected hydrophobic membrane system (ARS-HM).

Methane production in the electromethanogenic biocathode (Table 2) during the period without ARS-HM was on average $50 \pm 17 L_{CH_4} m^{-3} d^{-1}$, showing more instability than in the period with the ARS-HM connected and no statistically significant ($73 \pm 8 L_{CH_4} m^{-3} d^{-1}$). These values are in the same range of the ones obtained in previous work with the same set-up and similar feeding [11], although higher values have been reported [34–36]. Related to the amount of CO_2 introduced in the cathode compartment, the average yield was of $2 mL_{CH_4} L_{CO_2}^{-1}$. This yield could be improved by adjusting the amount of CO_2 in the cathode feeding solution or recirculating into the cathode compartment, since CO_2 was provided in excess to the system. Thus, this yield should be taken as an indicative value.

Although the average methane production was higher in the second period, with the ARS-HM connected, the cathodic methane recovery, r_{cat} , (Table 2) was similar to the one obtained in the first period, showing that electrons were diverted to produce methane proportionally to current density.

3.2. Ammonia Removal and Recovery

As a result of the current density increase when the ARS-HM was connected (Table 2, Figure 2), ammonia removal efficiency increased to 31% (21% when ARS-HM was not connected, $p < 0.05$), as shown in Table 3. The influent NH_4^+-N concentration of $1.5 \pm 0.3 g L^{-1}$ decreased to $1.3 \pm 0.1 g L^{-1}$ and $1.0 \pm 0.1 g L^{-1}$ with the ARS-HM disconnected and connected, respectively.

Table 3. Average values for current density, COD and ammonia removal efficiencies, and nitrogen flux transfer through the membranes.

Phase	NH ₄ ⁺ -N Removal Efficiency (%)	N Flux Through the CEM (g _N m ⁻² h ⁻¹)	N Flux Through the PTFE (g _N m ⁻² h ⁻¹)
1	21 ± 5	0.26 ± 0.09	-
2	31 ± 3	0.36 ± 0.11	0.28 ± 0.08

The average flux through the CEM was 0.26 g_N m⁻² h⁻¹ in the first period and increased 38% when the ARS-HM was connected, although this difference was not statistically significant. In turn, the average flux through the hydrophobic membrane (PTFE) was 0.28 g_N m⁻² h⁻¹, slightly lower than the flux through the CEM. The obtained values for the N flux through the CEM in the first period is half the 0.54 g N m⁻² h⁻¹ obtained in previous studies with a similar feeding substrate and the same configuration [4]. Regarding the N flux through the hydrophobic membrane, the obtained average value in this study is lower than previously reported by other authors, applied to anaerobic digestion technology. Although reported values are very variable, they are in a range from 1.48 g N m⁻² day⁻¹, using a membrane contactor to recover ammonia from anaerobically digested chicken manure [37]; to 89 g N m⁻² day⁻¹, submerging a gas-permeable membrane (expanded PTFE) in a vessel filled with swine manure [38]. However, previous work developed in our group with hydrophobic membranes for ammonia recovery has shown a similar value for N flux when operating the cathode compartment at pH values under 9.

Ammonia flux through hydrophobic membranes is concentration and pH dependent [37,39,40]. Previous works have reported that N flux increases in basic pH, since the ammonium-ammonia equilibrium displaces towards the last gaseous species, which is able to traverse the hydrophobic membrane [41]. The removal of ammonia from the cathode compartment helped to maintain a pH value close to neutrality, favorable for the electromethanogenic biomass. The catholyte pH during the ARS-HM connection phase was 7.7 ± 0.3, while the average pH was 1 point higher when the ARS-HM was disconnected in the first phase (8.8 ± 0.2, *p* < 0.05). Although the pH value was favorable for biomass development, it did not achieved values high enough to boost ammonia diffusion through the hydrophobic membrane. The *K*_a for ammonia dissociation at 23 °C is 9.30, so the fraction of deprotonated ammonia at pH values of 8.8 and 7.7 was 24% and 2%, respectively [42,43]. The proportion of recovered ammonia compared to migrated ammonium from the anode to the cathode compartment is low, but coincident to the fraction of protonated ammonia.

Differently to abiotic cathodes, electromethanogenic biocathodes need an optimum pH to develop its activity. Other authors have reported an optimal pH of 7.5 in an electromethanogenic biocathode, with the highest current density and methane production in the assayed pH range, between 6 and 8 [22]. In the present study, the catholyte solution contained a phosphate buffer in order to limit pH increase usually observed in MEC equipped with CEM [44]. This basification of catholyte pH is produced by H⁺ reduced migration from the anode to the cathode compartment due to other competing cations present in the substrate, such as NH₄⁺, K⁺ or Na⁺ [7,18,45].

Regarding the effect of ammonia concentration on N flux through the hydrophobic membrane, the average value in the catholyte was of 338 mg L⁻¹. In the 14 days of HMS operation, concentration in the acidic solution reached 317 mg_N L⁻¹, nearly equaling the concentration in the catholyte side, which represented a recovery of 6 mg_N d⁻¹, equivalent to 7.5 mg_{NH₃} d⁻¹ (Figure 3). In case cathode compartment would have been operated in batch mode, ammonia concentration would have probably increased and favor N flux through the hydrophobic membrane. However, as stated before for the pH value, ammonia concentration increase in the cathode compartment must be limited to avoid toxicity to electromethanogenic biomass developed in the biofilm.

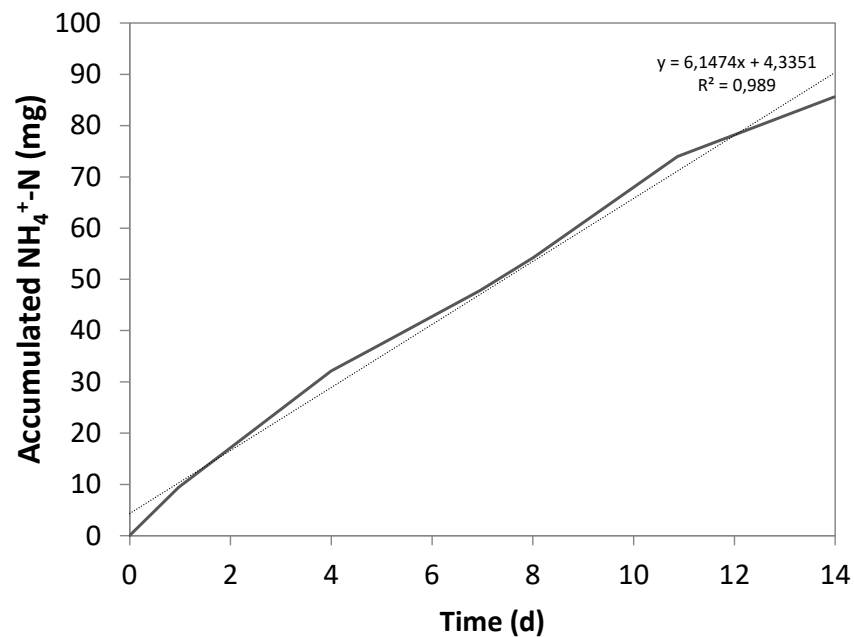


Figure 3. Accumulated NH₄⁺-N in the acidic solution during the ARS-HM operation.

3.3. Electromethanogenic Biocathode Coupled to Hydrophobic Membrane Evaluation

Figure 4 shows the average daily amount of charge (Q^-) produced in the MEC in both operation periods, compared to the amount of charge (Q^+) used for ammonia migration through the CEM and the amount derived to methane production (Q^-). Around 43% of the charge was used for ammonium migration in the first period, while during the second period, when the ARS-HM is connected, a slight decrease is detected (38%). On the other hand, between 23–27% of the charge was used in the cathode for methane formation. Other cations present in pig slurry digestate may take part in the migration of positive charges to the cathode compartment to maintain the electroneutrality [44,46]. It can be seen, then, that the amount of ammonium removed from the anode compartment and methane produced in the cathode are proportional to the amount of charge produced.

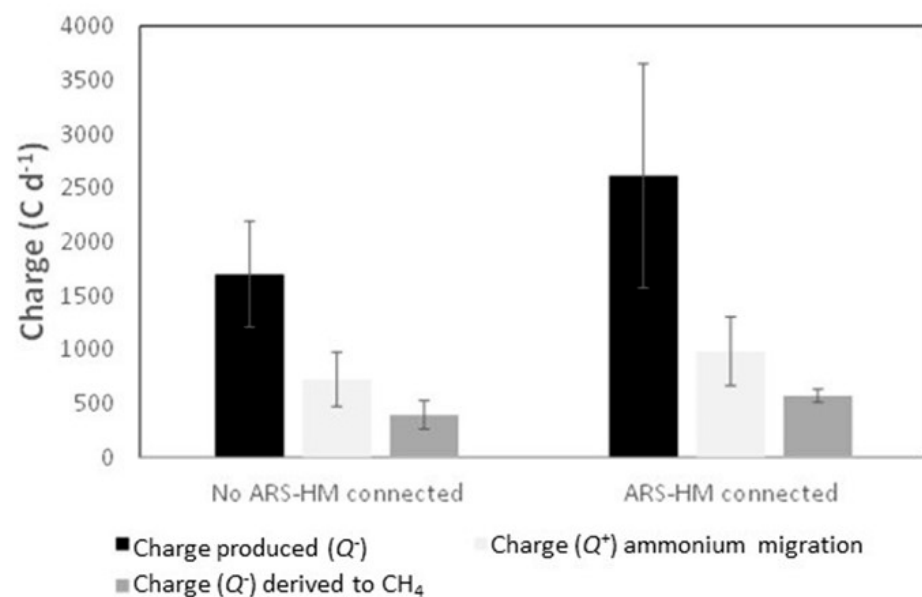


Figure 4. Comparison of the average daily charge production (Q^-) to the transport of charge in the form of ammonium (Q^+) transferred to the cathode compartment and the charge Q^- derived to methane production in the biocathode.

This charge (Q^-) is externally supplied and accounts for the energy required for biogas upgrading and ammonium migration. Energy consumption in this MEC, accordingly to the applied potential and the intensity produced, was on average of 45 kWh m^{-3} of methane produced. Previous work have reported energy consumption for methane production in electromethanogenic biocathodes of the same order of magnitude [11,15,47] and even values of $1 \text{ kWh m}^{-3} \text{ CH}_4$ in a medium-scale prototype [36]. For the migration of ammonium alone, the energy consumption was of 5 kWh kg^{-1} of removed N. In this case, of concomitant electromethanogenesis and ammonia removal in the same MEC, the reported energy consumption is shared by both processes.

There are several advantages of using hydrophobic membranes for ammonia recovery from electromethanogenic biocathodes, against stripping/absorption technology. On the first hand, although at a slow rate, N transfer is feasible at near to neutrality pH, with no need of alkali or temperature addition. A recent study has shown that operating hydrophobic membranes at moderate alkaline conditions would prevent inorganic fouling on the membrane surface, besides being economically viable for the treatment of domestic wastewater treatment [48]. On the second hand, previous studies have reported a clear improvement in nitrogen recovery when using membranes by reducing nitrogen losses, that potentially occurred via condense water in the gas phase of a stripping column [24]. Furthermore, energy requirements are reduced, since no aeration is required. Finally, hydrophobic membrane has been reported to prevent microorganisms transfer towards the absorbent, while air flow biomass from the biocathode could move with the gas flow and accumulate in the absorbent of the stripping system [24].

The MEC coupled to ARS-HM technology readiness level (TRL) presented in this study is TRL 4, since has been validated in lab-scale. However, other authors have developed medium [36] and pilot scale systems [49], for the assessment of MEC and methane production. Also real-scale reactors are being currently developed, as described in a comprehensive review recently published [20]. Besides, hydrophobic membranes are being assessed at pilot scale [50,51], thus it could be feasible to achieve a TRL 6 for the MEC ARS-HM in a few years. This evolution in the scaling-up of MEC technology and increase in the demand of materials such as electrodes or membranes will help to decrease investment costs, as shown in the different scenarios reported previously [52,53]. Scaling-up of the MEC coupled to ARS-HM will allow in the future to approach realistic economic evaluation of this technology.

4. Conclusions

The MEC coupled to the ARS-HM has shown as a feasible technology to achieve ammonia recovery, reduce organic matter content and upgrade biogas from digested pig slurry. The average nitrogen transference through the CEM was of $0.26 \text{ g}_N \text{ m}^{-2} \text{ h}^{-1}$, which represented 21% removal efficiency, while these values increased to $0.36 \text{ g}_N \text{ m}^{-2} \text{ h}^{-1}$ (although no statistically significant) and 31%, respectively, when the ARS-HM was connected in the catholyte recirculation loop. The removal of ammonia from the cathode compartment helped to maintain a lower pH value for the electromethanogenic biomass (7.69 with the ARS-HM, against 8.88 with no ammonia recovery) and boosted methane production from $50 \text{ L m}^{-3} \text{ d}^{-1}$ to $73 \text{ L m}^{-3} \text{ d}^{-1}$. Due to the high oscillation of methane production along the MEC operation, this increase was not statistically significant. The use of hydrophobic membranes for ammonia recovery is feasible at near to neutrality pH, avoiding energy consumption for aeration or heating, and organic contamination of the absorbent, compared to the conventional stripping/absorption technology.

Author Contributions: Conceptualization, M.C. and A.B.; methodology, M.C. and A.B.; formal analysis, M.C.; investigation, M.C. and L.B.; resources, A.B.; writing—original draft preparation, M.C.; writing—review and editing, M.C., L.B. and A.B.; supervision, A.B.; project administration, A.B.; funding acquisition, A.B. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

ARC	Ammonia recovery chamber
ARS-HM	Ammonia recovery system based on hydrophobic membrane
BES	Bioelectrochemical systems
CEM	Cation exchange membrane
COD	Chemical oxygen demand
HRT	Hydraulic retention time
MEC	Microbial electrolysis cell
MFC	Microbial fuel cell
NH ₄ ⁺ -N	Ammonia nitrogen
OLR	Organic loading rate
PTFE	Politetrafluorethylene
Q	Charge
SHE	Standard hydrogen electrode
TCD	Thermal conductivity detector
TRL	Technology readiness level

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