Hydrophobic membranes for ammonia recovery from digestates in microbial electrolysis cells: assessment of different configurations

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ABSTRACT

The combination of hydrophobic membranes and microbial electrolysis cells (MEC) was assessed in two different configurations in order to recover ammonia from anaerobically digested pig slurry. Politetrafluorethilene (PTFE) hydrophobic membranes were inserted both in an H-type three-chamber cell (MEC-H) and a two-chamber sandwich configuration MEC (MEC-S), both fitted with a cationic exchange membrane (CEM) dividing the anode and cathode compartments. The use of electrochemical techniques such as electrochemical impedance spectroscopy was applied to monitor the increase of the biofilm on the anode, related to the decrease of the charge transfer resistence. When operated in the higher organic loading rate (28±5 Kg COD m^{-3} d^{-1}) the current density produced in the MEC-H was 1.40±0.71 A m^{-2}, compared to 0.61±0.28 A m^{-2} in the MEC-S. The flux of ammonium through the CEM in the MEC-H was of 3.4±1.2 g N m^{-2} h^{-1}. Regarding the recovery of ammonia through the hydrophobic membrane, the flux of ammonia was of 1.5 and 0.7 g N m^{-2} h^{-1} in the MEC-H and MEC-S, respectively, mainly governed by the pH value and the ammonia concentration of the catholyte. The combination of MEC with hydrophobic membranes reveals as a suitable technology for the recovery of ammonia and treatment of high strength wastewater such as livestock manure.

Keywords

PTFE, livestock manure, nutrient recovery, bioelectrochemical systems, electrochemical impedance spectroscopy

1. Introduction

Waste and wastewater management technologies are evolving in the last years from the waste removal purpose towards the biorefinery concept. Biorefineries can recover nutrients and other products of interest from energetic crops, organic wastes and other waste fluxes [1], including sustainable management practices and closed cycle processes whenever possible. Wastes, whether industrial, domestic, agricultural, or from livestock are a great opportunity to recover water, energy, nutrients and chemical products, and have a big potential for application in biorefineries [2,3].

Bioelectrochemical Systems (BES) have emerged as a highly versatile technology that allows joining the treatment of wastewater to the production or recovery of energy carriers and compounds such as nutrients [4]. These devices take profit of exoelectrogenic microorganisms in order to catalyse oxidation and/or reduction reactions. There are several experiences of using BES in combination with other wastewater treatment technologies, such as anaerobic digestion, to close nutrient cycles or recover resources and energy [5–8]. The recovery of ammonia from high strengths wastewater (i.e. livestock manure) is one of the possible applications of BES and big efforts have been made to optimise the process [9,10]. In a circular economy approach, the recovery and reuse of ammonia from wastewater is a priority over its removal through technologies such as the nitrification-denitrification process [11]. Ammonia is a key component in fertilizing activities, and its recovery from waste streams will reduce the demand of ammonium produced by industrial processes.

Previous studies have demonstrated the suitability of BES for ammonia removal from wastewater using cation exchange membranes in dual chamber reactors, to promote the migration of cations from the anode to the cathode compartment thanks to the electron flux between both electrodes [12–16]. Several comprehensive and critical reviews have been published dealing with ammonia removal in BES [9,17,18], showing the great interest that

this technology arises. Once ammonia concentrates in the cathode compartment, a subsequent recovery step is needed [9]. A stripping and absorption unit can be coupled to the cathode compartment to easily recover the ammonium in an acidic solution [19,20] thanks to the high pH value promoted in the cathode compartment of a microbial electrolysis cell (MEC), which favour the volatilisation of ammonia [10,21,22]. However, the striping step needs continuous pumping of air, so it is energy consuming; other alternatives must be tested.

Recently, hydrophobic membranes made of polypropylene (PP), polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE), permeable to gases, are being applied to ammonia recovery, in the form of flat, tubular, or hollow fibre membranes [23–26]. This technology has been tested in anaerobic digestion [27–32] or from raw manure [33–37], among other substrates. Recovery efficiencies of more than 97% have been achieved in these assays. Ammonia gas dissolved in a waste stream or a substrate can traverse the pores of the hydrophobic membrane and react with an acidic solution placed on the other side, typically sulphuric acid, to form ammonium sulphate.

Pilot-scale demonstration plants have been reported for the recovery of ammonia from swine manure [38], poultry litter [35], from a wastewater treatment plant effluent [39], filtered anaerobic digestion effluent [40], or from rendering condensate wastewater [41]. Finally, full-scale nitrogen recovery plants based on gas permeable membranes have been implemented at Yverdon-les-Bains (Switzerland) wastewater treatment plant (WWTP) [42], Münster (Germany) WWTP [43] and at Wuppertal (Germany) Membrana GmbH (3M) production site for industrial wastewater treatment [44].

Great efforts are being made to understand the main parameters involved in ammonia transference through hydrophobic membranes and process modelling [25,31,45,46]. Among the most important issues to be addressed when working with hydrophobic membranes for

ammonia recovering are osmotic distillation, pore wetting and membrane fouling. The first process occurs as a consequence of the differences in vapour pressure between both sides of the membrane and leads to a continuous dilution of the acidic solution and the decrease in ammonia concentration [26,32,37]. Pore wetting makes membranes gradually less hydrophobic, and is one of the difficulties for fully scale this technology to industrial level [47]. Regarding fouling, it leads to deterioration of flux, an increase in power consumption, change in membrane hydrophobicity and a decrease in membrane lifespan [48]. New configurations and materials are being tested in order to improve membrane fouling and wetting resistance [49–51].

The use of these membranes coupled to the ammonium migration in a MEC could simplify and reduce the energy demand of the recovery step compared to the stripping and absorption process [52,53]. Furthermore, compared to the use of hydrophobic membranes in the anaerobic digestion process, the ammonia transference coupled to the MEC will be improved thanks to the high pH (>9) of the catholyte, that displace the ammonium/ammonia equilibrium to the last one gaseous species [21]. This way, no alkali addition or aeration [33,34] will be needed to maintain the driving force for the membrane separation process, reducing operation costs. Furthermore, the catholyte, which is in contact with the hydrophobic membrane, is a clean solution, with no organic neither particulate matter, avoiding membranes fouling.

Previous work has demonstrated that gas-permeable hydrophobic membranes can be successfully employed in a MEC for ammonia recovery from urine [52,54,55] or as a proton shuttle to improve the MEC performance [56]. New cell configurations have been proposed in order to up-scaling ammonia recovery MECs [57]. Also Electrochemical Systems (abiotic anodes) have been extensively employed in combination with hydrophobic membranes in last years [58–62]. However, there is a lack of studies about the coupling of these systems to

anaerobic digestion for the treatment of high strength wastewaters, such as livestock manure. In addition, system design improvements are needed to increase ammonia recovery in the acidic solution and simplify the operation of the reactor. The ammonia recovery system may be integrated in the recirculation loop of the catholyte, as the most used configuration up to now [52–54,63], or be integrated in the MEC in a three-compartments system. This last configuration may simplify MEC operation in a future scale-up of the system, reducing the number of vessels.

Finally, it is important to understand the relation between the bioelectrochemical performance of BES (due to its direct relation with ammonia transport through the CEM, the higher the current density the higher the ammonia transport) and anode colonisation by electrode-reducing microorganisms. In this regard, techniques such as cyclic voltammetry (CV) or electrochemical impedance spectroscopy (EIS) are being used to monitor biofilm development on bioanodes [64,65].

The aim of this study was to assess the recovery of ammonium and organic matter removal in a lab-scale MEC connected to a hydrophobic membrane system, as a technology to be applied to the treatment of organic and nitrogen high strength wastewater. The evolution of the biofilm developed on the anode of the MECs was also analysed through electrochemical techniques. Two different configurations were compared, (i) the direct integration of the hydrophobic membrane in the cathode compartment, and (ii) the integration of the hydrophobic membrane in the recirculation stream of the catholyte.

2. Materials and methods

2.1 Experimental set-up

Two different configuration MECs were used in the experiments, (i) an H-type 3 chambers MEC (MEC-H), where the hydrophobic membrane was integrated in the cathode

compartment; (ii) and a sandwich or flat plate configuration dual-chamber MEC (MEC-S), where a hydrophobic membrane system (HMS) was integrated in the recirculation stream of the catholyte.

The MEC-H consisted of three 0.6 L glass bottles connected with side openings (Figure 1a and b). A cation exchange membrane (CEM, dimensions: 20 cm^2; Ultrex CMI-7000, Membranes International Inc., Ringwood, NJ, USA) was placed between the side openings of the first and second (or middle) bottle (anode and cathode compartments, respectively). A piece of carbon felt (dimensions: 173 cm^2; thickness: 3.18 mm; Alfa Aesar GmbH and Co KG, Karlsruhe, Germany) was used as anode; and a 304 stainless steel mesh was used as cathode (dimensions: 173 cm^2; mesh width: 150 μm; wire thickness: 112 μm; Feval Filtros, Spain). A polytetrafluoroethylene (PTFE) flat membrane (0.45 μm pore size, Filter-Lab) was inserted between the second and third bottle (ammonia recovery compartment, ARC), achieving a free area of 10 cm^2. The ARC, were the acidic solution was placed, was equipped with a magnetic stirrer.

The MEC-S was a two-chamber cell (0.5 L each compartment), following the design described elsewhere [21] (Figure 1c and d). Two different materials were used as anode, depending on the feeding (i) granular graphite with diameter ranging from 1 to 5 mm (Typ 00514, enViro-cell Umwelttechnik GmbH, Oberursel, Germany), when a synthetic solution was used as anolyte; (ii) carbon felt (168 cm^2), with the same characteristics than the MEC-H, when digestate was used as anolyte. The same stainless-steel cathode and CEM (168 cm^2 each one) as in the MEC-H was used in the MEC-S. This way, the surface of the MEC-H CEM represented 12% of the MEC-S CEM, calculated as the ration between CEM areas, $CEM_{MEC\text{-}H}/CEM_{MEC\text{-}S,}$ because of the different system configuration.

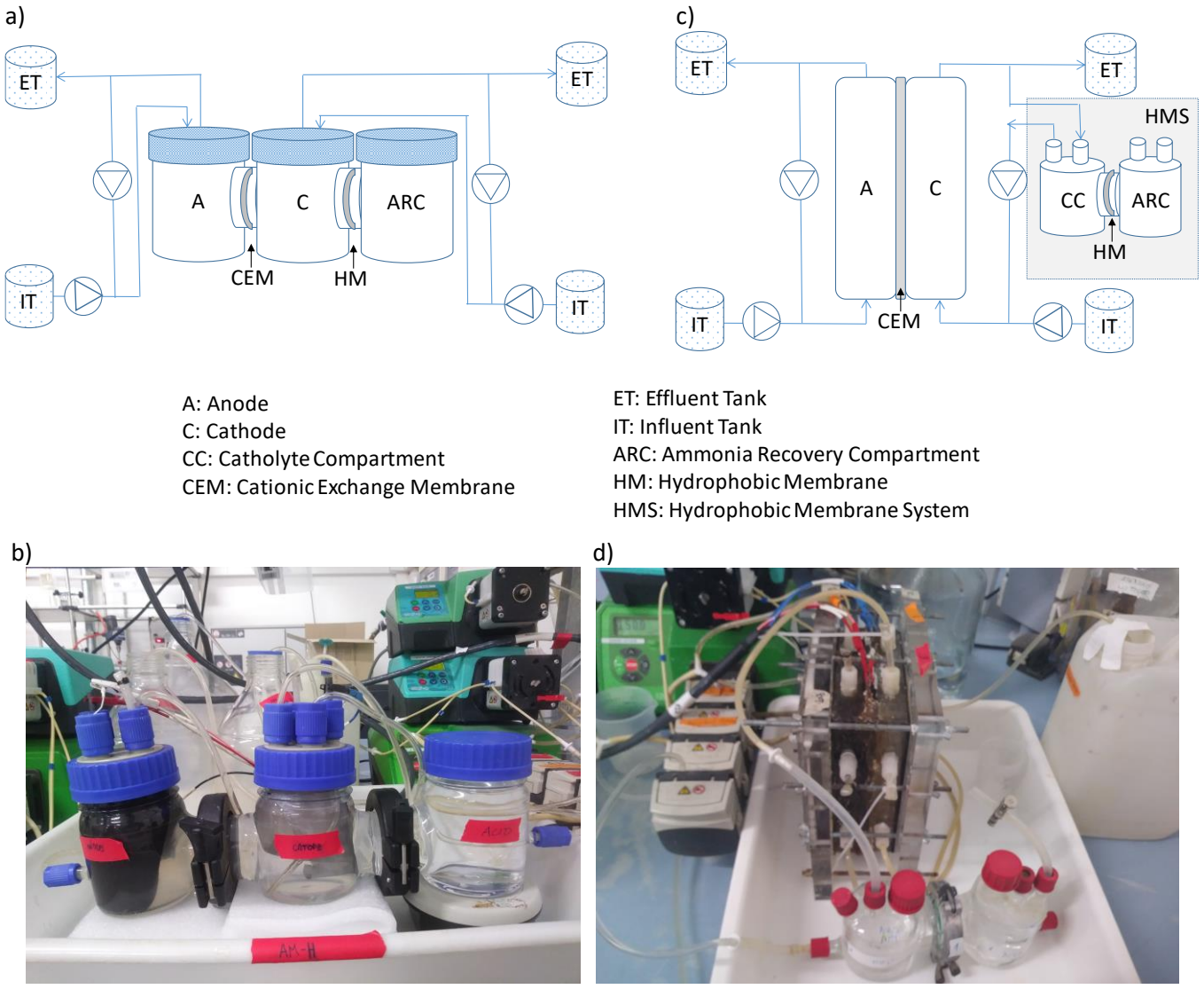

Figure 1. Scheme (a) and picture (b) of the MEC-H, and scheme (c) and picture (d) of the MEC-S with the HMS connected.

For the MEC-S, a hydrophobic membrane system (HMS) was integrated in the catholyte recirculation stream to recover the ammonium transferred from the anode to the cathode compartment. Two glass bottles (0.25 L each one) with a side opening were connected, inserting a PTFE membrane between them as described before (10 cm^2). One of the chambers was filled with catholyte, while the second chamber was filled with an acidic solution (H_2SO_4, 1.8 M). Both chambers were equipped with a magnetic stirrer.

A potentiostat (VSP, Bio-Logic, Grenoble, France) was used to poise the anode (working electrode) potential to 0 mV in a three-electrode mode, with an Ag/AgCl reference

electrode (Bioanalytical Systems, Inc., USA; +197 mV vs. standard hydrogen electrode, SHE) inserted in the anode compartment of each cell. 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 MEC-S anode compartment synthetic feeding solution (COD of 2.2 g_{O2} L^{-1} and 1 g_{NH4+-N} L^{-1}) contained (per litre of deionized water): CH_3COONa, 2.9 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. The solution of trace mineral contained (per litre of deionized water): $FeCl_3 \cdot H_2O$, 1.50 g; H_3BO_3, 0.15 g; $CuSO_4 \cdot 5H_2O$, 0.03 g; KI, 0.18 g; $MnCl_2 \cdot 4H_2O$, 0.12 g; $Na_2MoO_4 \cdot 2H_2O$, 0.06 g; $ZnSO_4 \cdot 7H_2O$, 0.12 g; $CoCl_2 \cdot 6H_2O$, 0.15 g; $NiCl_2 \cdot 6H_2O$, 0.023 g; EDTA, 10 g. This composition was chosen to simulate a diluted pig slurry regarding COD, ammonia content and alkalinity.

The digestate used to feed the anode compartment of the MEC-S and the MEC-H was collected from a lab-scale thermophilic anaerobic digester, which was fed with pig slurry. The digestate was stored at 6º C until its use and sieved (125 µm). The sieved digestate (pH of 8.1±0.2, COD of 21.9±3.3 g_{O2} L^{-1} and NH4+-N of 1.9±0.3 g L^{-1}) was diluted with tap water to achieve the different organic loading rates used during the experiment (Table 1).

The cathode compartments were fed with a NaCl 0.1 g L^{-1} solution.

2.3 Reactors operation

2.3.1 HMS batch assays

In a first block of experiments, in order to characterise the NH_4^+-N flux through the PTFE membrane, a series of batch assays were performed with the HMS alone, before connecting it to the MEC-S.

The catholyte compartment was filled with a synthetic 500 mg L^{-1} NH_4^+-N solution at three different pH values (10, 11 and 12), simulating the composition of the cathode effluent. This NH_4^+-N concentration was chosen as the one expected when the MEC-S was to be fed with digestate, accordingly to previous work [21]. A lower concentration, of 125 mg L^{-1} NH_4^+-N, was also assessed at pH 11 to simulate the conditions expected in the synthetic operation of the MEC-S. The pH values were adjusted with NaOH to the desired value at the beginning of the experiment, without any regulation throughout the assay. The acid compartment (ARC) was filled with H_2SO_4, 1.8 M.

Each batch lasted for 48 h, and started filling both compartments with the corresponding solution and switching on the magnetic stirring. Samples were taken from both compartments at time 0, 3, 6, 24, 31 and 48 h. Once a batch was finished, the compartments were emptied and rinsed with deionised water before starting the following one. The different conditions were tested in triplicate.

2.3.2 Continuous synthetic fed MEC-S assay

Regarding the MEC-S operation, the anode compartment was inoculated with graphite granules from the anode of a lab-scale mother MEC operated with synthetic medium containing acetate. The MEC-S with no HMS inserted was operated for 1.5 years before starting these assays, so it was considered that the biofilm was mature.

The MEC-S with the HMS was operated for 190 days. 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 feeding velocity of the cathode compartment was reduced from day 105 to 14 mL h^{-1}, to favour the increase of ammonium concentration in the catholyte. The hydraulic retention time (HRT) of each compartment was of 12.6 h, 20.6 h and 10.3 h for the anode, cathode and HMS 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 7.83 kg_{COD} m^{-3} day^{-1}. These HRT were increased the last 85 days of operation for the cathode and HMS catholyte compartments to 36.6 h and 18.3 h, respectively. The acidic solution of the ARC was replaced when it became saturated with ammonia. Samples of the anode and cathode compartment effluents and from the ARC were taken on weekdays. The MEC-S was operated at room temperature during the entire assay (23±2 ºC).

2.3.3 Continuous digestate fed assays

Before starting the operation with digestate, the granular graphite anode of the MEC-S was replaced with carbon felt to avoid clogging due to suspended solids content of the new feeding. Both the MEC-S and the MEC-H anodes were inoculated with the anode compartment effluent from a lab-scale MEC operated with synthetic solution. Both reactors were operated in continuous with synthetic solution in a start-up period until current density production stabilized. After 26 days of operation, the influent was switched to diluted digested pig slurry. The dilution was stepwise decreased, from 3 times diluted digestate (1 L digestate: 2 L water) to undiluted digestate, to adapt the anode biofilms to increasing OLR and nitrogen loading rate (NLR), accordingly to Table 1. The MECs were operated with digested pig slurry for 115 days. On day 57, the cathode compartments of both cells were switched from

continuous to batch mode operation to improve the conditions for ammonia diffusion through the hydrophobic membrane. The acidic solution of the ARC was replaced when it became saturated with ammonia, monitoring the solution pH. Sampling of the anode and cathode compartments effluents and from the ARCs started after switching to 1.5 diluted digestate, and was performed on daily basis. Both MECs were operated at room temperature during the entire assay (23±2 ºC).

Table 1. Organic (OLR) and nitrogen (NLR) loading rates of the MECs in the different phases of digestate operation.

Phase	Period (d)	OLR (Kg_{COD} m^{-3} d^{-1})	NLR (Kg_{NH4+-N} m^{-3} d^{-1})
1	0-25	6±1	1.0±0.2
2	26-36	9±2	1.0±0.2
3	37-74	15±2	1.5±0.2
4	75-115	28±5	2.9±0.4

2.4. Analytical methods and calculations

Ammonium nitrogen (NH_4^+-N) and pH were determined in the anolyte and catholyte effluent and acidic solution samples. 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). NH_4^+-N was analyzed by a Büchi KjelFlex K-360 distiller (Büchi Labortechnik AG, Flawil, Switzerland), capture of distillate in boric acid and subsequent titration with 0.1 M HCl with a Metrohm 702 SM autotitrator (Metrohm AG, Herisau, Switzerland). Chemical oxygen demand (COD) was determined in anolyte feeding and effluent samples. All the analyses were performed following Standard Methods [66].

The current density (A m^{-2} or A m^{-3}) of the MECs was calculated as the quotient between the intensity recorded by the potentiostat (A) and the area of the anode (m^2) for MEC-S and MEC-H (carbon felt); or the net volume of the anode compartment (m^3) for the MEC-S (granular graphite in synthetic operation). Ammonium and COD removal efficiencies in the MECs were calculated as the ratio of the difference between the anode compartment influent

and effluent concentrations and the influent concentration. Ammonium recovery efficiency in the acidic solution was calculated as the ratio between the amount of ammonium removed from the anode compartment in a day and the ammonium accumulated in the acidic solution in the same period. Regarding batch test, for HMS characterisation, recovery efficiency was calculated as the ratio between the amount of ammonia found in the acid compartment at the end of the assay and the initial amount of ammonia in the catholyte compartment. Ammonia flux through the membranes, expressed in the form of ammonium nitrogen, NH_4^+-N, (g N m^{-2} h^{-1}) was calculated as the ratio between the amount of ammonium nitrogen transferred (g) and the elapsed time (h) and the membrane surface (m^2).

2.5. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetries (CV) were performed periodically on the MECs to characterise the anodic biofilm development, on days 0, 20, 26, 36, 56, 69, 77, 90 and 106. Both techniques were carried out using a potentiostat equipped with an impedance module (VSP, Bio-Logic, Grenoble, France). EC-Lab software (V11.20, Biologic Science Instruments) was used for instrument control and data analysis. The measurements were done in a three-electrode mode, with the same configuration as described in the Experimental set-up Section. EIS test were performed at an AC signal amplitude of 10 mV, between 100 kHz and 10 mHz. CV was carried out at a scan rate of 1 mV s^{-1}, and with an amplitude between -0.1 and -0.6 V.

The Randles equivalent circuit shown in Figure 2 was used to fit EIS data and identify parameters dominating electrical behaviour at the bioanodes. This equivalent circuit model consisted of an ohmic resistance component (R_{ohm}), followed by an electrochemical charge transfer resistance (R_{ct}) in parallel with a double layer constant phase element (CPE). The CPE is used instead of a capacitor to simulate the non-ideal behaviour of distributed

capacitance, typical of porous electrodes [67]. No Warburg diffusion element was included in the circuit, since no tails related to diffusion phenomena were generally detected.

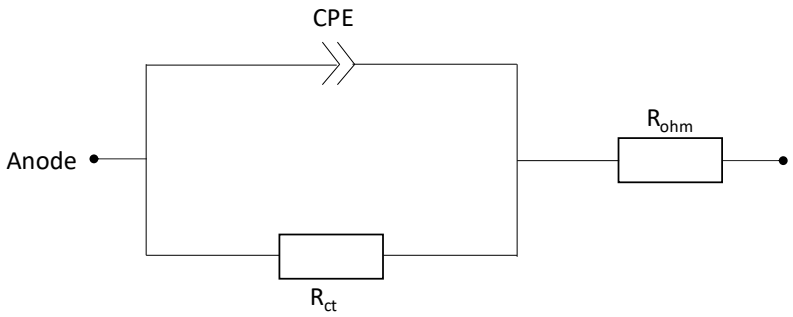

Figure 2. Equivalent circuit used for the analysis of impedance of the anodic biofilm (CPE, constant phase element; R_{ct}, charge transfer resistance; R_{ohm}, ohmic resistance).

EIS data were plotted in Nyquist plots, expressing the real (Z_{re}) and the imaginary impedance (Z_{im}) in the horizontal and vertical axis, respectively. The intercept of the curve with the real impedance (Z_{re}) axis at the highest frequencies (left side of the axis) has been considered as the ohmic resistance (R_{ohm}) and the Z_{re} value of the lowest frequency (where Z_{im}=0) has been considered as the total R_{int} [68]. The magnitude of the Nyquist arc qualitatively yields the charge-transfer (R_{ct}) resistance of the anode.

3. Results and discussion

3.1. Performance of the HMS

The HMS characterisation (Figure 3) showed that ammonia removal efficiency from synthetic catholyte in 48 h achieved 94±2%, 93±5% and 100±1% at pH 10, pH 11 and pH 12, respectively, when using an initial concentration of NH_4^+-N of 500 mg L^{-1}. The efficiency achieved 99±1% when using an initial concentration of NH_4^+-N of 125 mg L^{-1} with a pH of 11. Although these high removal efficiencies, the recovery efficiencies in the acid compartment increased with the pH (73±3%, 75±2% and 89±2% at pH 10, pH 11 and pH 12, respectively) but were lower than the removal efficiencies, probably due to ammonia

volatilisation phenomena in the catholyte compartment due to the basic pH values. In the case of an initial concentration of NH_4^+-N of 125 mg L^{-1} with a pH of 11, the recovery efficiency was of 81±5%, slightly higher than that for the equivalent pH and 500 mg L^{-1} initial concentration. Ammonia transfer rate through the hydrophobic membrane was of 12.7±0.3, 13.1±0.4, and 14.1±0.4 g N m^{-2} h^{-1} at pH values of 10, 11, and 12, respectively, while it decreased to 3.4±0.7 g N m^{-2} h^{-1} with the initial concentration of 125 mg L^{-1} with a pH of 11. The obtained results agree with the observations of other studies, which reported an increase in ammonia flux through tubular gas permeable membranes when increasing pH or ammonium concentration of the substrate [25,30,49,69,70].

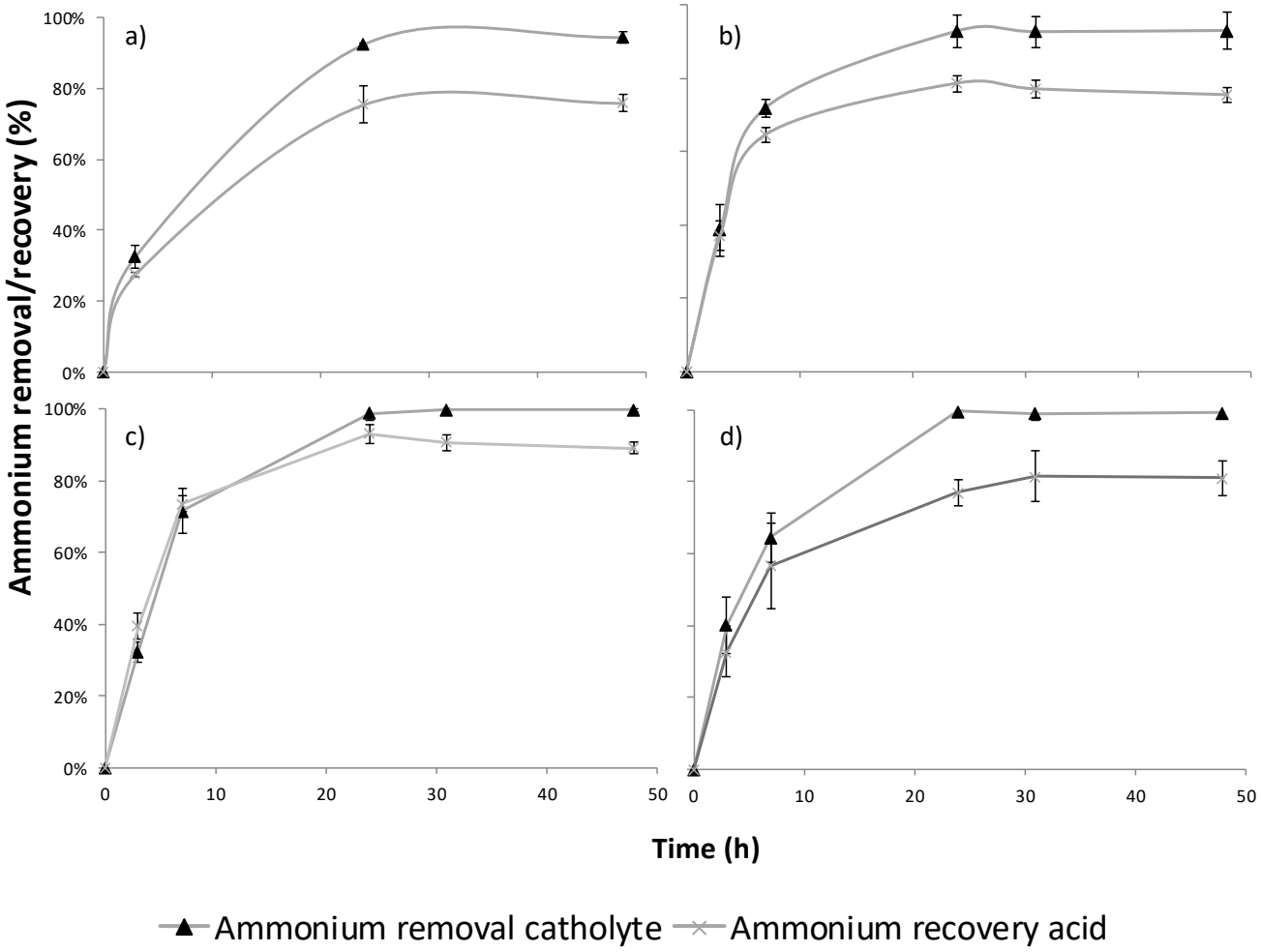

Figure 3. Ammonium removal and recovery efficiency in the catholyte and acid compartment in the HMS, with an initial NH_4^+-N concentration of 500 mg L^{-1} at a) pH 10, b) pH 11 and c) pH 12; and d) with an initial NH_4^+-N concentration of 125 mg L^{-1} and pH 11.

3.2. Performance and removal efficiencies of the MEC-S with synthetic feeding

The HMS was connected in the recirculation circuit of the catholyte of the MEC-S after the characterisation of the ammonia flux through the hydrophobic membrane (section 3.1). The MEC-S produced an average current density of 47±25 A m^{-3} (Figure 4), with a COD and an ammonium removal efficiency in the anode compartment of 85±4% and 25±6%, respectively. Maximums of 40% ammonium removal efficiency were achieved in the periods with the highest current density (over 100 A m^{-3}). The improvement in the current density during the last 20 days of operation allowed for an average ammonium recovery efficiency of 33±5%, representing an average flux of 0.3 g N m^{-2} h^{-1}. Ammonium removal efficiency is closely related to the behaviour of the current density, as previously reported [21]. The cathode effluent contained 25±6% of the ammonia fed to the anode compartment. The amount of ammonia recovered in the acid compartment of the HMS was fluctuating, with an average of 7±3%, which represents a recovery of 29±17% of the N transferred from the anode to the cathode compartment. Previous reports have shown an unstable transport across the hydrophobic membrane. Zamora et co-workers (2017) operated a urine-fed scaled-up MEC for ammonia recovery, achieving 31±11% nitrogen removal from the anode chamber [54]. The cathode was connected to a trans-membrane chemisorption (TMCS) module for ammonia recovery. In that case, the average pH measured in the cathode was 9.0±1.2 so, due to this high fluctuation in the catholyte pH, NH_3 was not always the dominant species and the transport over the TMCS was unstable (31±59%). The removal and recovery values obtained in that study are very similar to the results achieved in the synthetic operated MEC-S. Other studies have reported similar ammonium removal efficiencies, but achieving higher recovery efficiencies, such as Kuntke and co-workers (2016), who achieved an average ammonium-nitrogen removal of 42±6% in a continuous urine feed MEC, recovering in a punctual period of 5 days about 95% of the N removed from the anolyte in sulphuric acid [52]. In that study,

catholyte pH was 9.5±0.2, so the higher pH stability, added to the fact that the cathode compartment was operated in batch mode -achieving higher catholyte ammonia nitrogen concentration, over 800 mg L^{-1}-, may have enhanced ammonia absorption in the acid solution.

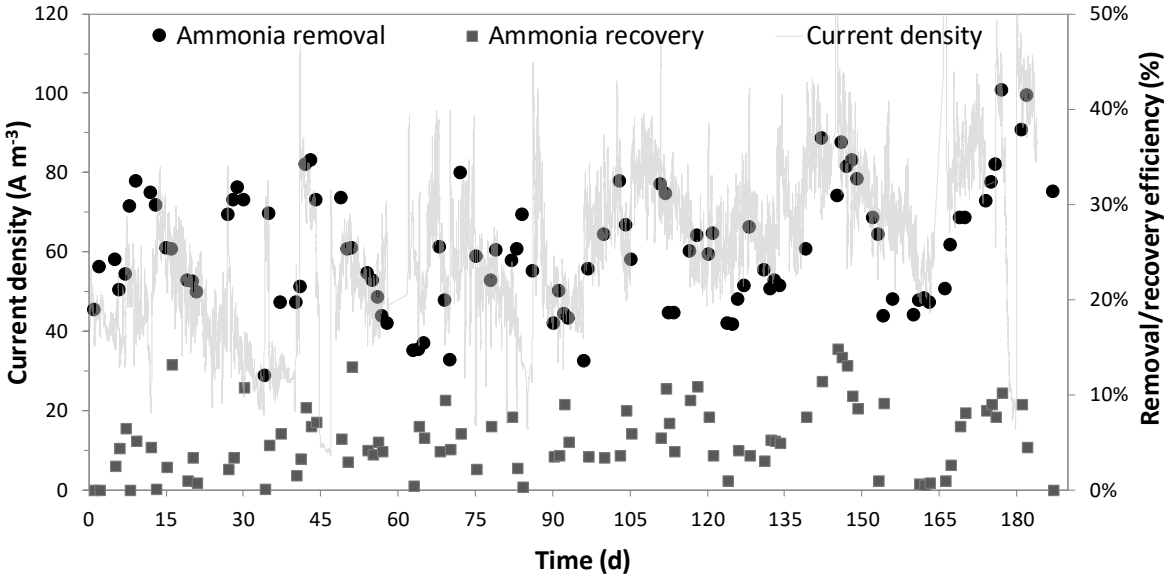

Figure 4. Current density obtained with the operation of the MES-S in synthetic operation, ammonia removal efficiency from the anode compartment and recovery efficiency in the acid compartment of the HMS.

As shown in Figure 4, ammonia recovery efficiency was higher in the periods with higher current density, since more ammonia is transferred to the cathode compartment and a higher pH value is achieved [22]. In these conditions, up to 48% of the ammonia transferred to the cathode compartment was recovered, with a maximum flux of 2.9 g N m^{-2} h^{-1}, slightly lower to the result obtained in batch with the lower ammonium concentration (3.4±0.7 g N m^{-2} h^{-1} with the initial concentration of 125 mg L^{-1} with a pH of 11). Furthermore, the increase of the HRT of the catholyte compartment also increased the N flux through the hydrophobic membrane, since pH and ammonium concentration of the catholyte increased. The average flux through the hydrophobic membrane for the first 105 days of operation was of 1.1±0.7 g N m^{-2} h^{-1}, showing a high fluctuation, concomitant to a pH value of the cathodic bulk solution

of 11±1 and a N concentration of 112±33 mg L^{-1}. When the HRT was increased, the average flux increased 27% (1.4 ±0.9 g N m^{-2} h^{-1}, pH of 10±1 and N concentration of 270±98 mg L^{-1}).

3.3. Operation of the MECs with digestate feeding

3.3.1 Performance and COD removal efficiency

The operation with digested pig slurry of both MECs was started after inoculation and operation for a short period with synthetic media (data not shown) and the OLR and NLR was stepwise increased (Table 1). The current density obtained in MEC-H reactor gradually increased with the increase in OLR in each phase, especially in phase 4 (Figure 5a). The reference electrode had a malfunction between the day 96 and 104 during which no real data of the voltages and current intensity was provided by the potentiostat. After replacement of the reference electrode, the system quickly recovered its performance in terms of current density. Regarding the MEC-S, Figure 6a shows a more unstable performance in current density production than MEC-H, and in phase 4 the potential applied by the potentiostat was not constant because of overpotential in the system. In average, current density in the first 3 phases were similar in both reactors, as shown in Table 2, while the performance in phase 4 improved especially in the MEC-H, which achieved an average of 1.40±0.71 A m^{-2}, compared to 0.61±0.28 A m^{-2} in the MEC-S. Previous work of a MEC in sandwich configuration operated with digested pig slurry and a similar OLR achieved similar values for current density, 1.59 ± 0.70 A m^{-2} [21]. The average COD removal efficiency achieved 21±7% and 16±6% in the MEC-H and the MEC-S, respectively. The decrease in COD removal efficiency with respect to the synthetic operation with acetate in the MEC-S (which achieved a COD removal efficiency of 85%) is consistent with previous studies with pig slurry digestate or food and agricultural wastes used as complex substrates [21,71], since simple substrates such as acetate are easier to degrade [72].

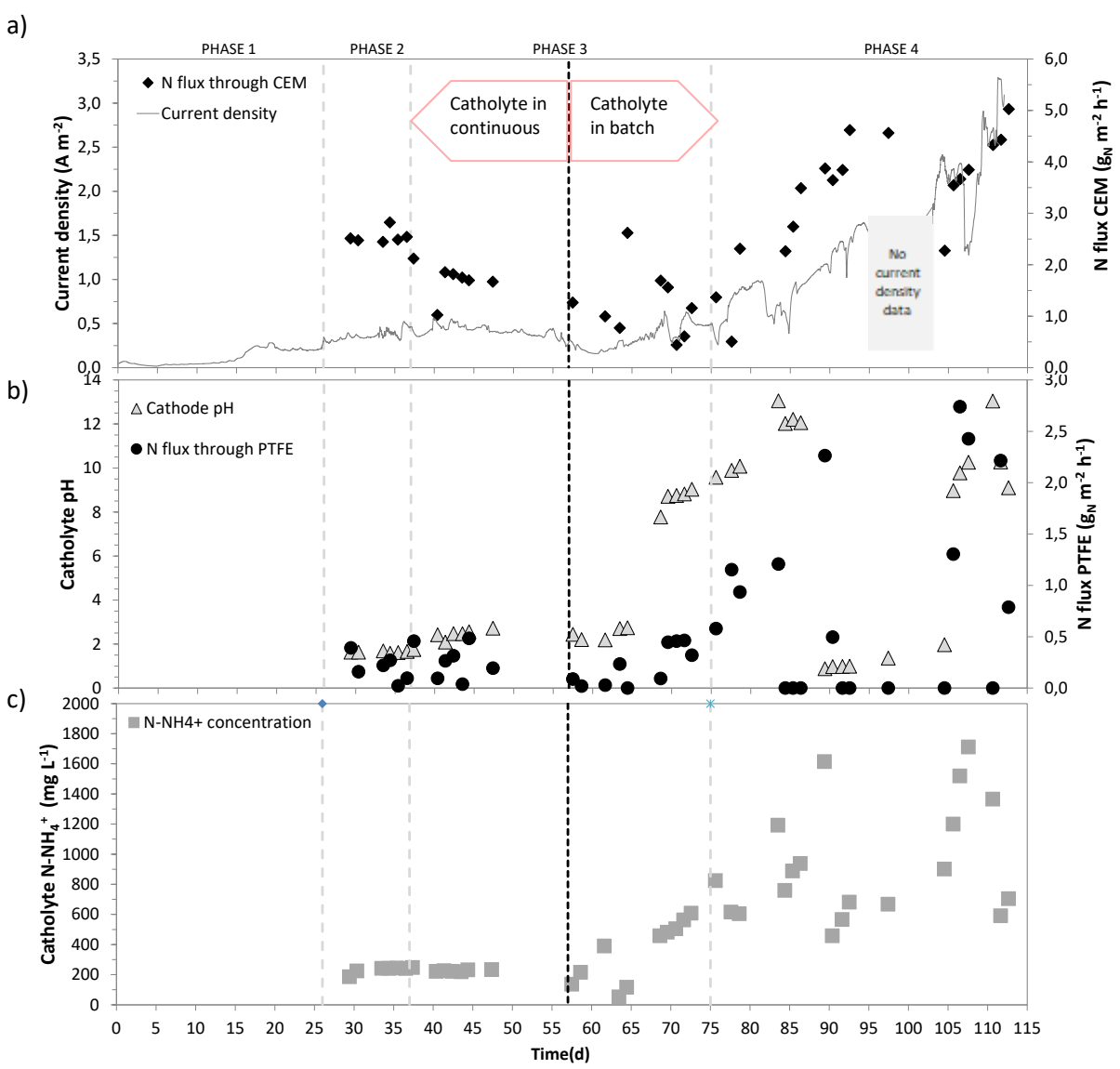

Figure 5. Current density obtained with the operation of the MES-H in digestate operation and nitrogen flux through the cationic exchange membrane (CEM) (a); nitrogen flux through the hydrophobic membrane (PTFE) and pH of the cathode compartment bulk solution (b); and nitrogen ammonium concentration in the cathode compartment bulk solution (c). The reference electrode had a malfunction on day 96 and was replaced on day 104, so data in this period was omitted in the figure.

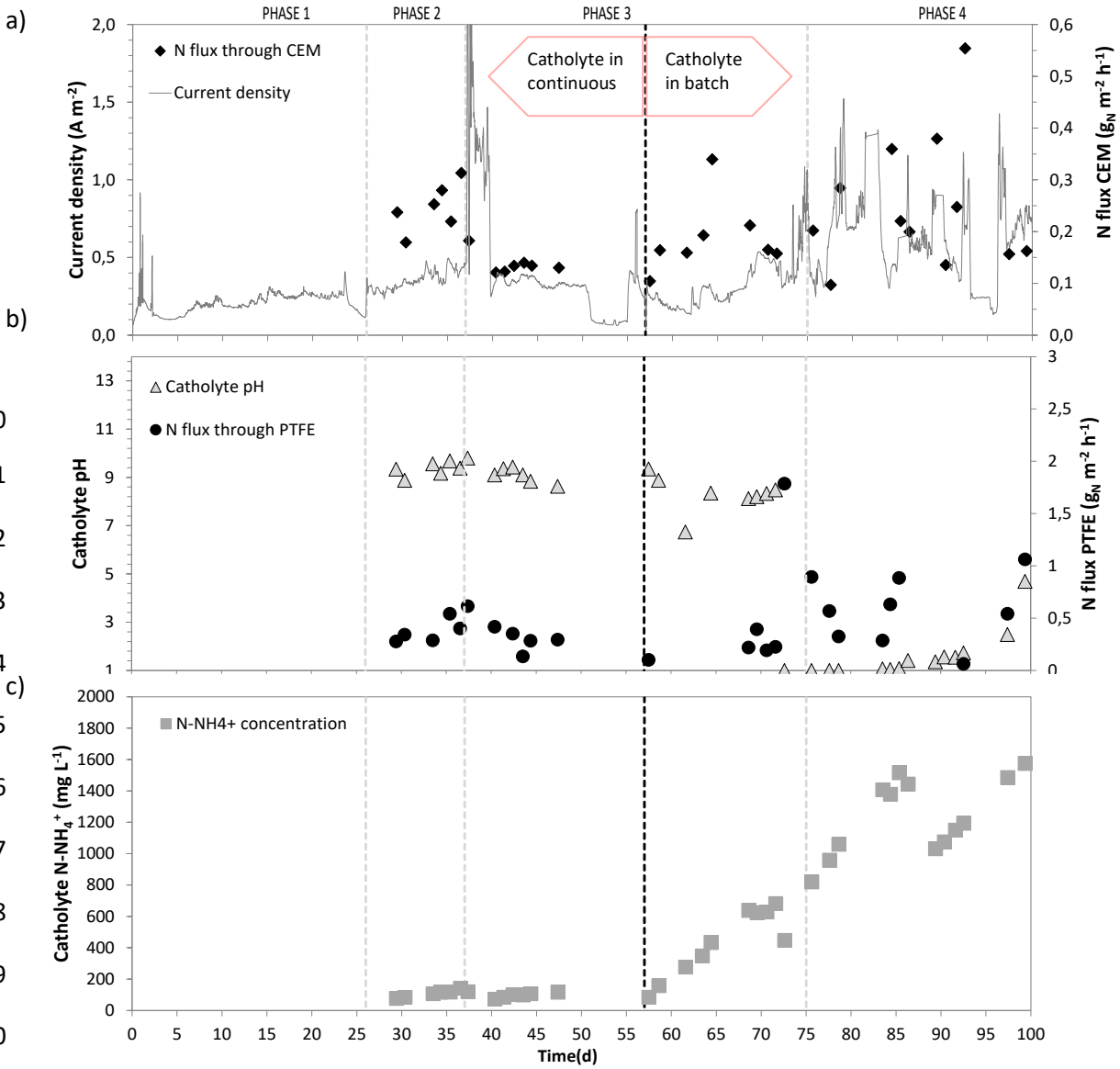

Figure 6. Current density obtained with the operation of the MES-S in digestate operation and nitrogen flux through the cationic exchange membrane (CEM) (a); nitrogen flux through the hydrophobic membrane (PTFE) and pH of the cathode compartment bulk solution (b); and nitrogen ammonium concentration in the cathode compartment bulk solution (c).

3.3.2 Ammonium removal efficiency

Ammonium removal efficiency in the MEC-H achieved 23±1%, 17±3% and 18±5% in phases 2, 3 and 4, respectively, compared to slightly lower values in the MEC-S (20±8%, 13±2% and 7±3% in phases 2, 3 and 4, respectively). The NH_4^+-N flux by migration from the anode to the cathode compartment in the MEC-H (Figure 5a) was in general an order of

450 magnitude higher than in the MEC-S (Figure 6a), achieving 3.4±1.2 g N m^{-2} h^{-1} in phase 4
451 (Table 2). These results can be explained by the different CEM surface in each reactor. As
452 stated in the Materials and Methods section, the surface of the MEC-H CEM represented 12%
453 of the MEC-S CEM, because of the system configuration. Therefore, with a similar current
454 density, a similar amount of N was transferred through the CEM of both reactors, despite the
455 smaller surface in the MEC-H CEM.

456 Ammonium removal in MEC is dependent on the current density, as described before
457 [12]. In this study, a chronoamperometric operation mode was chosen, which involves poising
458 the anode to a certain potential. If desired, to avoid oscillations in current density and N flux,
459 a chronopotentiometric method could be also applied, fixing the current density in the external
460 circuit. In this second option, anode potential may be less favourable for exoelectrogenic
461 bacteria, since will change to a value dependent on several factors, including the substrate
462 type and concentration, the applied voltage, and the specific microorganisms present [73].
463 This could lead to lower COD removal efficiencies.

464 For a fixed current, various cations (generally Na^+, K^+, Mg^{2+}, Ca^{2+}) in the anolyte can
465 compete with the NH_4^+ ions for transport across the CEM, thus potentially compromising the
466 removal of NH_4^+ ions from the anolyte [74]. This phenomena has been extensively studied
467 previously with raw and digested pig slurry, showing that NH_4^+ acts as a primary charge
468 carrier, accounting for 53%-67% of the migrated positive charges [75,76].

469 The flux through the CEM obtained in the MEC-S is half the 0.54 g N m^{-2} h^{-1} obtained
470 in previous studies with the same feeding substrate and configuration [21]. Differently, the
471 high flux in the MEC-H is very similar to the one obtained with a submersible microbial
472 desalination cell fed with synthetic solution [77].

473

Table 2. Main operational results (average ± standard deviation) of the MECs during digestate feeding (CEM: cationic exchange membrane; HM: hydrophobic membrane).

Phase		Current density ($A\ m^{-2}$)	NH_4^+-N transference through the CEM ($g\ m^{-2}\ h^{-1}$)	NH_4^+-N transference through the HM ($g\ m^{-2}\ h^{-1}$)	NH_4^+-N concentration in the cathode compartment ($mg\ L^{-1}$)	pH cathode compartment
MEC-S						
1		0.20±0.07	-	-	-	-
2		0.36±0.07	0.25±0.05	0.4±0.1	107±24	9.3±0.3
3	Cathode in continuous	0.37±0.35	0.16±0.06	0.3±0.2	105±26	9.2±0.4
	Cathode in batch			0.6±0.7	510±153	8.3±0.1
4		0.61±0.28	0.25±0.13	0.7±0.3	1238±243	1.8±1.1
MEC-H						
1		0.16±0.08	-	-	-	-
2		0.35±0.06	2.6±0.1	0.2±0.1	230±23	1.6±0.1
3	Cathode in continuous	0.38±0.11	1.4±0.6	0.3±0.2	218±34	2.4±0.3
	Cathode in batch			0.3±0.2	461±129	8.6±0.5
4		1.40±0.71	3.4±1.2	1.5±0.8	937±384	10.8±1.5

Although other ammonia removal technologies, such as stripping and absorption [78,79], membrane distillation [80,81] or ionic exchange [82,83] have reported higher removal efficiencies (>90%) than the obtained in this study, MEC present several advantages over them. MEC operation generates the favourable pH for ammonia volatilisation with no chemical addition nor temperature increase, differently from stripping and absorption process. If digested pig slurry was operated directly with membrane distillation, also an increase of pH, either by chemical addition or aeration, or temperature increase, would be needed to improve removal efficiency. Regarding ion exchange, a previous step of solids and organic matter removal would be needed to avoid clogging of the columns, and it is a process that has to be operated by repeating adsorption and regeneration cycles in order to remove and recover ammonia. Furthermore, ion exchange is more efficient at relative low pH (value of 6) [84], while digested pig slurry used in this study had a pH value of 8.

3.3.3 Ammonium recovery efficiency

NH_4^+-N flux through the hydrophobic membrane towards the recovery acid compartment presented a high variability in all the phases in both reactors, as shown in Figure 5b (MEC-H) and Figure 6b (MEC-S). NH_4^+-N average transference increased from 0.2 and 0.4 g N m^{-2} h^{-1} in phase 2 in MEC-H and MEC-S, respectively, to 1.5 and 0.7 g N m^{-2} h^{-1} in phase 4 (Table 2). Two factors had influence in these results: ammonia concentration in the cathode compartment and the pH of the bulk solution, as seen in the batch and continuous synthetic assays in this paper, and the results reported by other authors [34,69,70]. The pH value in the MEC-H cathode compartment was very low until half of phase 3 (Figure 5b), when the cathode compartment was operated in continuous mode. From day 57 on, the operation was switched to batch, in order to maintain a higher ammonia concentration in the cathode compartment (Figure 5c) and improve the N transference. This change also allowed for the increase in pH value, making it more favourable to the increase in the proportion of ammonia species. This way, NH_4^+-N in the cathode compartment increased from 230±23 mg L^{-1} in phase 2 to 937±384 mg L^{-1} in phase 4 (Table 2). In the case of the MEC-S, pH value in phase 2 and 3 was over 8 (Figure 6b), and althoug NH_4^+-N in the cathode compartment was half the value obtained in MEC-H in phase 2 and 3 (Figure 5c and Figure 6c), the NH_4^+-N flux through the hydrophobic membrane was similar or slightly higher. The switch from continuous operation to batch mode also allow for an increase in the NH_4^+-N cathode concentration, from 107±24 mg L^{-1} in phase 2 to 1238±243 mg L^{-1} in phase 4 (Table 2). This higher concentration may have improved the flux, due to the increase of the mass transfer driving force. Both reactors had a sharp decrease in the pH value in phase 4 after a change of the acidic solution in the recovery compartment, which drastically decreased the ammonia transference through the hydrophobic membrane until the pH increased to basic values. This behaviour was also observed during the sinthetic MEC-S operation, but in that case the pH

514 decrease was overcome in one or two days after the acid change and the recovery efficiency
515 recovered. The low pH of the new acid may promote, in the first hours after acid replacement,
516 a high diffusion of the catholyte ammonia through the hydrofobic membrane, and a pH
517 decrease. Although ammonium accumulated stepwise in the cathode compartment when
518 batch operation started, the concentration decreased following acid replacement (Figure 5c
519 and 6c). This adverse effect could be reduced with the circulation of the acid in a bigger tank,
520 in order to minimise the frequency of the acid substitution, or by the substitution of part of
521 the acid instead of the full recovery compartment.

522 Maximum flux through the hydrophobic membrane in the MEC-H was 66 g N m^{-2}
523 day^{-1}, concomitant to a pH value of the cathode bulk solution of 9.8 and an NH_4^+-N cathode
524 concentration of 1520 mg L^{-1}. This value is comparable to the one obtained in the MEC-S
525 with synthetic feeding. The N flux through the hydrophobic membrane achieved by other
526 authors, applied to anaerobic digestion technology, is very variable. It is in a range from 1.48
527 g N m^{-2} day^{-1}, using a membrane contactor to recover ammonia from anaerobically digested
528 chicken manure, operated with in sweep gas mode instead of using an acidic solution in
529 contact with the membrane [70]; to 89 g N m^{-2} day^{-1}, submerging a gas-permeable membrane
530 (expanded PTFE) in a vessel filled with swine manure [33]. Table 3 shows a compilation of
531 N flux reported in previous studies, working with different substrates and reactors.

532 Comparing both experimental configurations operated in this study, the 3 chamber
533 MEC (MEC-H) has achieved better results regarding current density and N flux through the
534 hydrophobic membrane than the MEC-S. Furthermore, the 3 chamber cell configuration is
535 less complex than other experimental setups using gas recirculation [21,85,86] or a multiple
536 absorption vessel [22]. It neither needs producing any overpressure to achieve the diffusion
537 over a membrane contactor [52]. Hence, it reveals as an interesting configuration for further
538 investigation and operation inprovement. For example, continuous pH control and

539 automatised acid replacement would be necessari in the ARC to achieve a more stable
540 ammonia flux through the hydrophobic membrane.

541

542 **Table 3.** Compilation of N flux through hydrophobic membranes reported by previous studies. (MEC: Microbial electrolysis
543 cell; EC: Electrochemical cell; PTFE: polytetrafluoroethylene; ePTFE: expanded polytetrafluoroethylene; PP:
544 polypropylene; PDMS: polydimethylsiloxane.)

Substrate	Reactor/tank	Kind of membrane	Nitrogen flux ($g\ m^{-2}\ day^{-1}$)	Reference
Anaerobically digested pig slurry	MEC	Flat PTFE	66	This study
Anaerobically digested pig slurry	Tank	Tubular ePTFE	28	[36]
Anaerobically digested pig slurry	Tank	Tubular ePTFE	6	[28]
Anaerobically digested pig slurry	Tank	Tubular ePTFE	6	[28]
Anaerobically codigested pig slurry	Tank	Tubular ePTFE	60	[87]
Anaerobically digested pig slurry	Tank	Tubular ePTFE	6.6	[32]
Anaerobically digested dairy manure	Tank	Tubular ePTFE	51	[69]
Anaerobically digested chicken manure	Tank	Tubular PDMS	1.48	[70]
Poultry litter	Tank	Flat ePTFE	17.78	[35]
Swine manure	Tank	Tubular ePTFE	89	[33]
Swine manure	Tank	Tubular ePTFE	2.27	[34]
Swine manure	Tank	Tubular ePTFE	38	[38]
Swine manure	Tank	Tubular ePTFE	27.1	[37]
Urine	EC	Flat PTFE	94	[53]
Synthetic wastewater	EC	Flat PTFE	69	[61]
Centrate of anaerobically digested sewage sludge	Tank	Tubular ePTFE	133	[88]
Urine	EC	Flat PP	1010	[60]

545

546

3.4. Electrochemical characterisation of the anode biofilm development

The development of the anode biofilm of both MECs operated with digested pig slurry was evaluated through two monitoring tools, EIS tests and CV. Figure 7 shows the anode EIS spectra (Nyquist plots) observed in different days of operation both for the MEC-H and the MEC-S (see Supporting Information SI1 for a description of the curves observed and Figure SI1 and Figure SI2 for Bode plots).

Using the equivalent circuit shown in Figure 2, the R_{ct} of the anodes at different stages of the microbial growth was evaluated from the EIS data obtained on different days. On day 20, were estimated to be 30.8 Ω and 16.8 Ω in the MEC-H and the MEC-S, respectively. This value decreased 89% during MEC-H operation, while only 16% in the MEC-S (Figure 8). This indicates that the microbial growth on the anode has a beneficial effect on the kinetics of the bio-electrochemical reaction as it decreases the anode activation losses due to increased biocatalyst density [89]. The reduction of the R_{ct} of the MEC-H anode is inversely proportional to the current density produced by the cell (R^2=0.9204). This correlation was not observed in the MEC-S, although periods with higher R_{ct} corresponded in general with less current density production. The slight increase in R_{ct} during MEC-S operation, observed also in other studies [89] may be due to an increase in inactive biofilm for electrochemical reactions.

The evolution of the anode CV overtime was also assessed (Figure SI3) to compare with the information provided by the EIS tests. The MEC-H showed a clear increase in the current generated by the oxidation reaction with time, while the MEC-S showed lower current production than the MEC-H and a poorer improvement over time. The evolution of the CV in both reactors pointed to the proliferation of the anode-reducing microorganisms, consistent with the data obtained with the EIS test, and showing the different behaviour of both reactors.

571 In summary, the electrochemical methods used in this study showed that an increase
572 in current density coincided with a progressive decrease of the anode internal resistance, as
573 described before [64].

574

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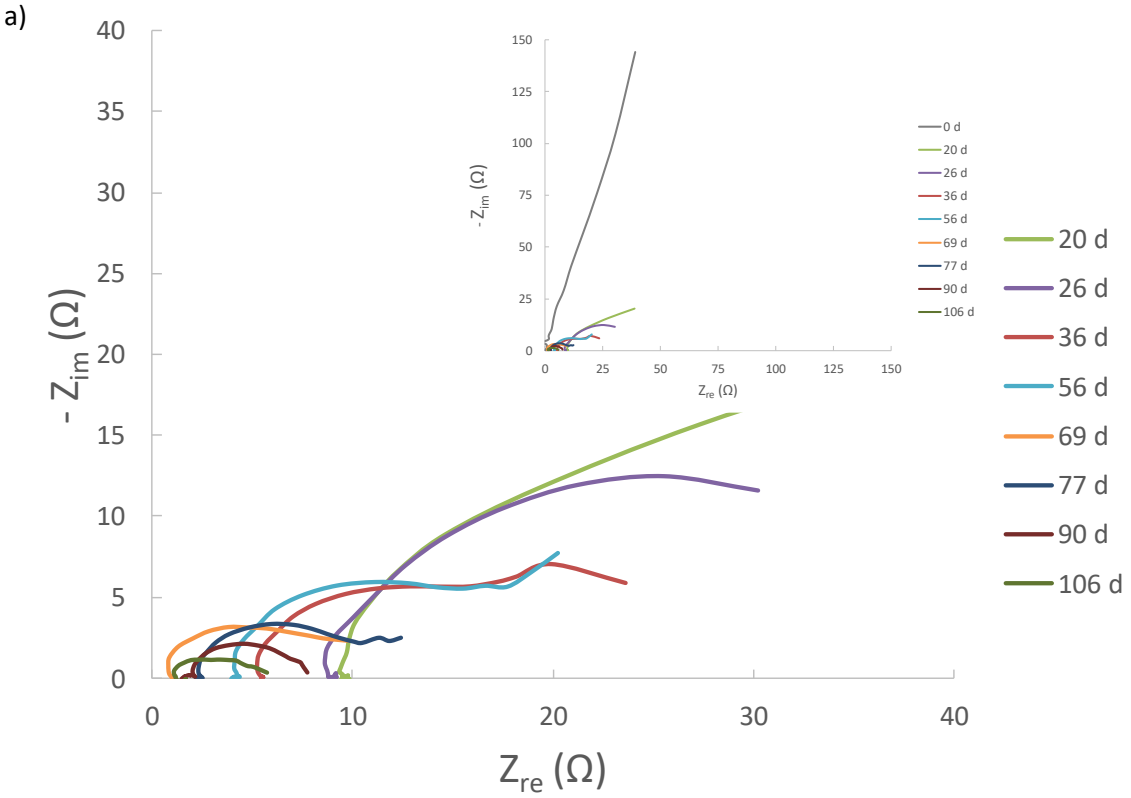


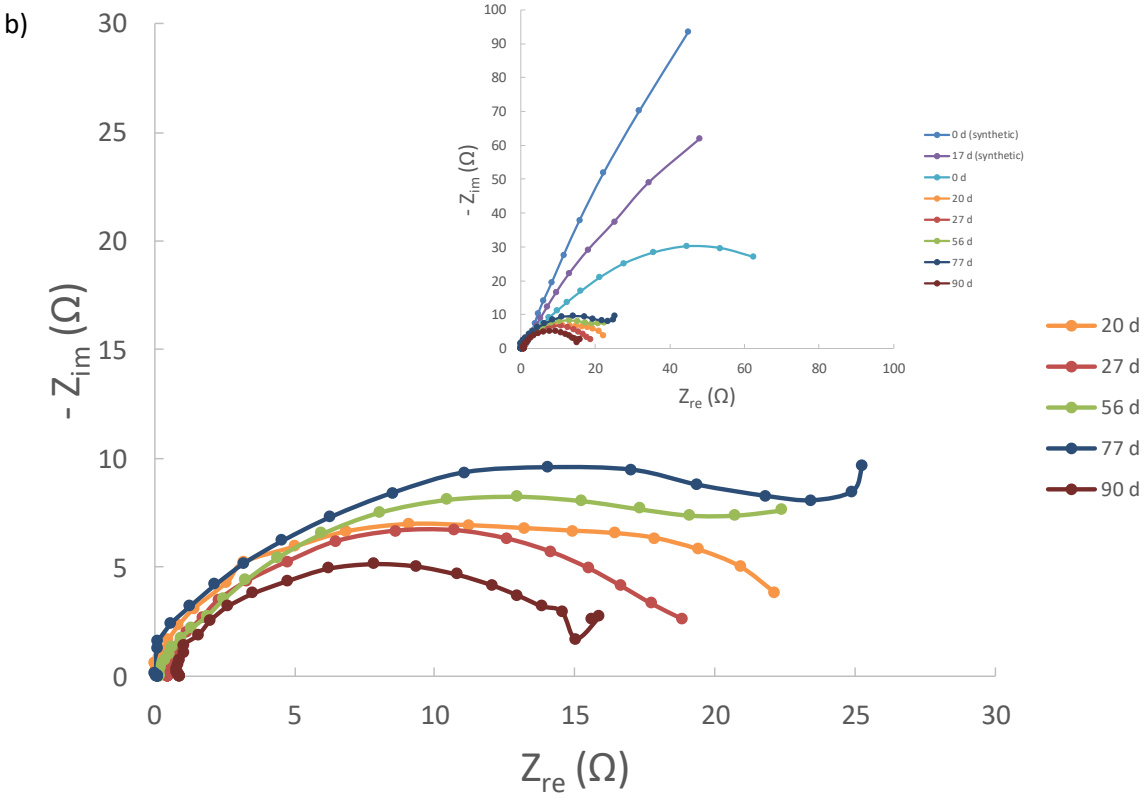
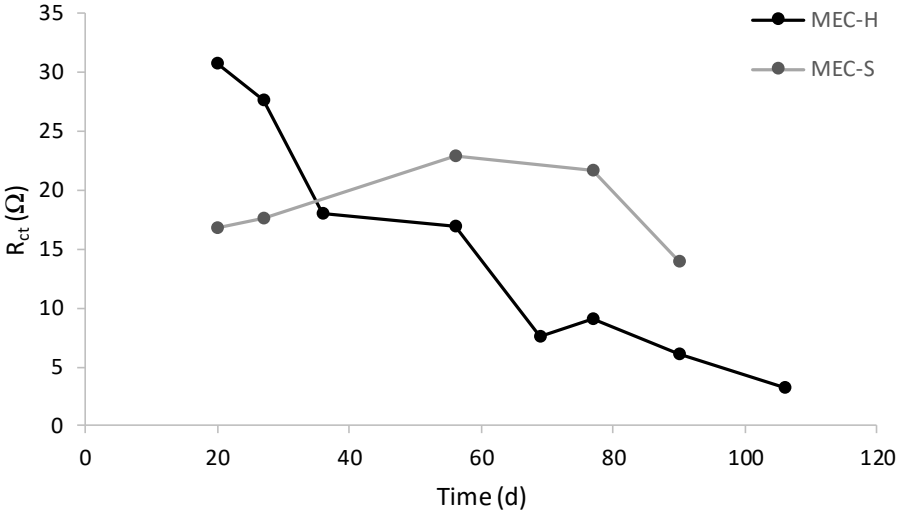


Figure 7. Anode electrochemical impedance spectroscopy spectra observed during 20-106 days of MEC-H operation, and including day 0 in the inset (a). And during 20-90 days of MEC-S operation, including day 0 and day 17 in synthetic operation and day 0 with digestate feeding in the inset (b).



582

583 **Figure 8.** Evolution of the R_{ct} in the MEC-H AND MEC-S.

584

585 ## 4. Conclusions

586 The combination of MECs with hydrophobic membranes reveals as a suitable
587 technology for the recovery of ammonia and treatment of high strength wastewater such as
588 livestock manure, either in a configuration with the membrane in contact with the cathode
589 compartment or in the catholyte recirculation circuit. Ammonia removal from the substrate
590 was directly linked to the current density produced by the cell, which in turn was correlated
591 to the development of biofilm in the anode. This biofilm evolution has been monitored by
592 electrochemical techniques (CV and EIS test) and its relationship with the anode resistance
593 has been assessed. In turn, the diffusion of ammonia through the gas permeable membranes
594 was enhanced with the catholyte ammonium content and pH, achieving a maximum flux of
595 66 g N m^{-2} day^{-1}. The evolution of the cathode pH during MEC operation avoids the addition
596 of alkali or aeration, compared to the direct use of hydrophobic membranes in anaerobic
597 digestion. Compared to a stripping and absorption system coupled to MECs, the use of
598 hydrophobic membranes for N recovery avoids electricity consumption for air pumping.
599 Furthermore, the 3-chamber cell configuration (MEC-H) simplifies the operation of the

recovery of ammonia, but improvement is still needed to stabilise the flux of ammonia through the hydrophobic membrane, highly dependent on catholyte and recovery acid pH.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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